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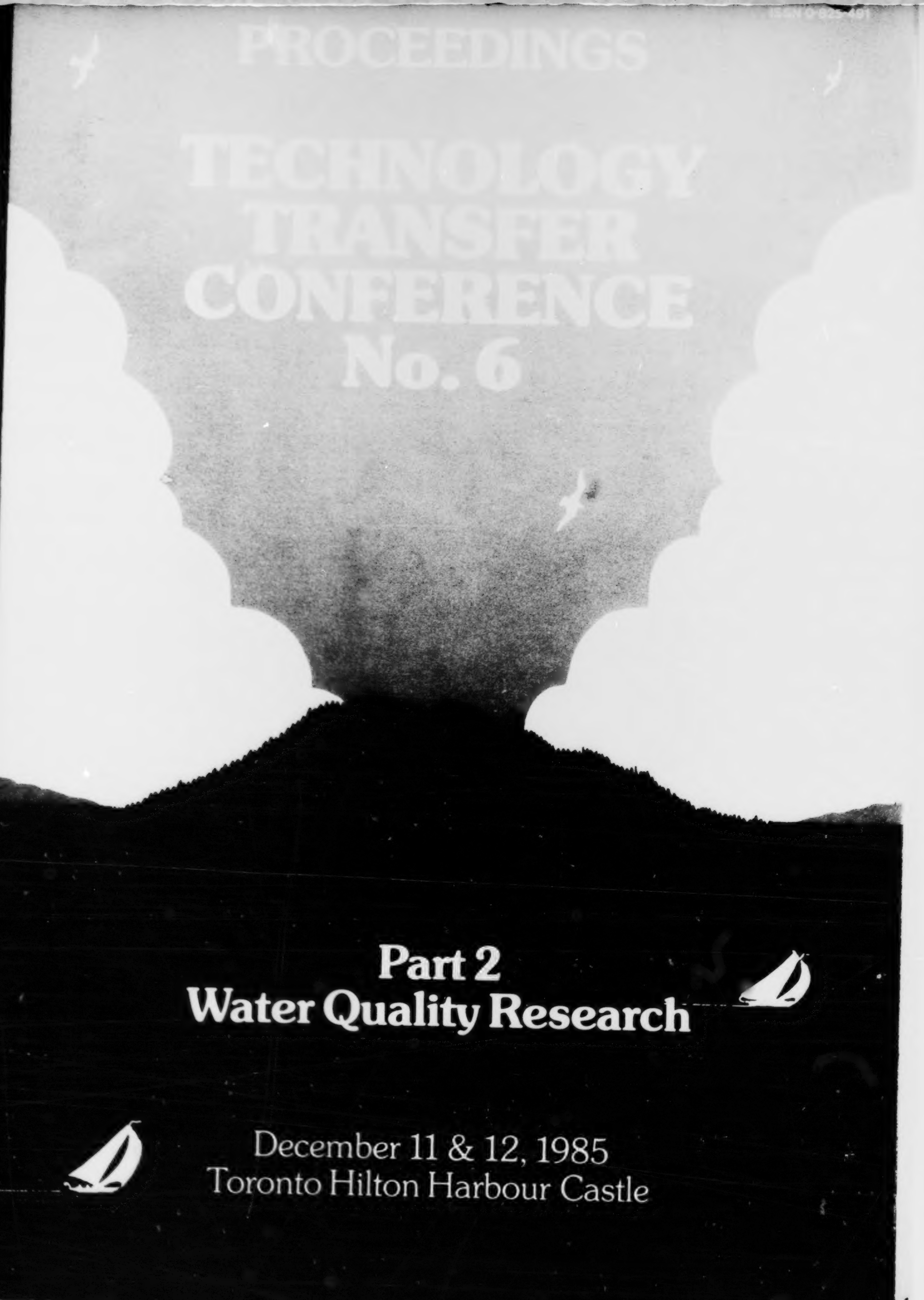

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE
No. 6

Part 2
Water Quality Research

December 11 & 12, 1985
Toronto Hilton Harbour Castle

ISSN 0-825-491

PROCEEDINGS

TECHNOLOGY TANSFER CONFERENCE NO. 6

December 11 & 12, 1985

Toronto Hilton-Harbour Castle

PART TWO

WATER QUALITY RESEARCH

Organized by
Research Advisory Committee

Sponsored by

Policy & Planning Branch
Ministry of the Environment
Ontario

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Organization Committee would like to thank the invited speakers, investigators and the National Research Council of Canada for their valuable contributions.

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INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at Technology Transfer Conference No. 6, held in December 1985 are presented in Conference Proceedings. These Proceedings are divided into three parts corresponding to the conference sessions - Part 1 deals with air quality research, Part 2 with water quality research, and Part 3 with liquid and solid waste research. Papers dealing with analytical methods and instrument development are assigned to each of the three parts.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Co-ordination Office at (416) 965-5788.

TOXICOLOGICAL EVALUATION OF GREAT LAKES DRINKING WATER

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ABSTRACT

A scientifically sound and defensible basis for the evaluation of human health effects requires a thorough knowledge of two elements: the toxicity of the chemical or process in question, particularly as it applies to humans, and the exposure to the chemical or process in question to which the average person or a specific group of persons is subject.

Many chemicals are found in the Great Lakes and many of these are not removed by filtration or other methods of purification. In addition, several chemicals are added to water or formed during the purification process and the potential hazard of these needs to be assessed.

This paper will address the significance of chemicals found in drinking water from the Great Lakes in several ways which will include the following:

- Estimation of exposure for water and other sources;
- The toxicological database available for the chemicals found in the Great Lakes;
- The assessment of the significance of the toxicology database in regard to human health;
- The significance of epidemiological evidence of health effects.

The presentation will stress methodology and will be illustrated through the use of case histories.

- DRAFT

TOXICOLOGICAL EVALUATION OF GREAT LAKES DRINKING WATER

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INTRODUCTION AND BACKGROUND

The quest for pure drinking water is deeply rooted in the history of mankind. Urbanization, even before the Birth of Christ, brought with it the need to develop means for water purification. It is recorded in Sanskrit medical lore and early Egyptian inscriptions that various means were devised to purify water including boiling and sand filtration. The learned medical philosopher Hippocrates drew attention to the importance of pure water in the maintenance of good health and he too prescribed procedures for water purification.

The first clear proof that public water supplies served as a vector for human disease came from the studies of Dr. John Snow in London and were based on his critical epidemiological observations of the London cholera outbreak of 1854. Numerous additional outbreaks of human disease including typhoid fever and cholera, in North American and Europe occurred during the 1800's. It was not until the turn of the century that slow sand filtration proved to be a critical step in eliminating or at least substantially decreasing the incidence of water-borne infections.

While filtration proved to be a reasonably effective means of disease control, the introduction in 1908 of chlorination as a means of ensuring bacteriological quality of water provided a milestone in water treatment technology. This is evidenced, for example, by the incidence of typhoid fever in Wheeling, West Virginia which fell from approximately 175 cases per 100,000 to 7 cases per 100,000 after the introduction of chlorination in 1918. Chlorination, therefore, was considered the panacea in terms of the maintenance of drinking water quality. With the discovery, however, of the role of chlorination in the formation of trichloromethanes, coupled with the application of sophisticated analytical methodology capable of demonstrating minute quantities of pesticides and environmental contaminants in drinking water, water treatment technologies have been subjected to intense scrutiny by scientists and politicians alike. Whereas at the turn of the century the risk/benefit equation strongly favoured the practice of chlorination, it having been successfully used to control the incidence of microbial infection, questions are being raised and societal attention is now focussed on the problem of residues of potentially toxic chemicals in municipal drinking water supplies.

Societal expectations regarding drinking water quality suggest that even minute risks are not readily tolerated and clean-up of surface water sources coupled with the introduction of improved water treatment technologies is now the accepted long-term goal. It is against this background that I wish to discuss with you today some of the issues that relate to the present quality of drinking water from the Great Lakes and some direction I see will be necessary to ensure an adequate supply of potable water in future years. I have chosen to discuss the Great Lakes basin partly because it represents and portrays a wide spectrum of important generic public health issues related to drinking water. But also because of the extensive population that is served from municipal water treatment facilities around its perimeter, it is also important to maintain a constant vigil on these bodies of water.

THE REGULATION OF DRINKING WATER SUPPLIES

A brief recapitulation of existing regulations relating to water supplies is essential to understanding were we are today and were we are headed. At present there is no Federal statutory authority governing the quality of drinking water supplies except for that which is implied in the Health and Welfare Act. Under the general provisions of this legislation, Federal authorities have drafted and published Canadian Drinking Water Guidelines which serve as a useful benchmark for establishing acceptable standards and guidelines in other jurisdictions. Under existing legislation the Province of Ontario develops guidelines for drinking water quality as well. Non-government organizations such as the WHO and in the United States, the National Academy of Sciences, have also addressed the problem of drinking water quality and regularly publish guidelines and/or toxicity profiles on chemical substances detected in drinking water.

The process of establishing guidelines requires the evaluation of toxicity and analytical data on chemicals found in drinking water. Where the toxicity and/or epidemiological data are adequate, acceptable human exposure limits may be established, when warranted, and translated into analytical standards which specify the maximum acceptable concentration of the particular contaminants in water. Problems encountered in this process include deficiencies in the toxicity and analytical data base which preclude the establishment of the nature and magnitude of risk associated with particular substances. These so-called "data gaps" pose significant problems because of the need to conduct research on the toxicology of substances prior to carrying out a risk assessment. I will deal with this problem in some depth later on.

Another special problem that arises in the risk assessment of chemicals in drinking water relates to estimation of risk posed by substances possessing carcinogenic properties. Whereas it is accepted practice in risk assessment to use safety or uncertainty factors in translating the results of animal toxicity studies to the human population this practice is considered by most authorities to have substantive limitations when applied to carcinogenic substances because of uncertainty regarding establishment of safe exposure levels for carcinogens. Newer concepts based on the growing knowledge base in carcinogenesis would suggest the virtually safe exposure levels can be estimated from studies in animals, however, it is generally agreed that these are not without some measure of risk even at very low doses. The concept of acceptable risk is therefore implicit in the establishment of guidelines for carcinogenic substances in drinking water even though these risks may be so minute as to be immeasurable and probably insignificant from the public health point of view. Epidemiological data, as we shall see, has, to date proven of limited values in the establishment for guidelines for drinking water, except, of course, in those cases where such data, gleaned from occupational settings, may be extrapolated to lower levels of human exposure. The need for improved methods to assess risks from chemicals in drinking water is therefore a matter of some urgent concern.

THE STATUS OF GREAT LAKES DRINKING WATER

The status of Great Lakes drinking water has been the subject of numerous recent studies. Included among these are the reports of the Committee on Assessment of Health Effects of Great Lakes Drinking Water, of the Quality of the Great Lakes Water Quality Review Board and the report of the Local Toronto Board of Health which documented the quality of the City of Toronto water supply. An ongoing study is currently being conducted under the auspices of the Canadian Public Health Association. I have been involved with this assessment of the quality of drinking water in 31 Canadian and United States municipalities located on the perimeter of the Great Lakes. The results of this study will be available early in the new year.

Of all of the studies currently available one consistent fact emerges. There are very few instances in which existing drinking water guidelines are exceeded in those municipalities examined to date. This is true even in those jurisdictions such as the St. Clair River and the Niagara River where levels of contamination are reported to be highest. Indeed, in the recently released joint report of Environment Canada and the Ministry of the Environment on Pollution of the St. Clair River, it is noted that the Ontario Drinking Water Surveillance Program indicated that no samples of drinking water exceeded Ontario objectives for this site nor were dioxins or dibenzofurans found in any sample of drinking water.

As I pointed out previously the establishment of water quality objectives is impeded, in part, by a lack of information on the toxicity of chemicals found in Great Lakes water. However, adequate data to conduct a provisional risk assessment do exist for certain substances currently not subjected to guidelines. A perusal of this group of substances leads to the conclusion that, in very few instances do the levels in drinking water exceed detection limit of analytical techniques. In those instances where the detection limit is exceeded, the values are generally low and exceedences occur only sporadically, probably due to specific local instances of contamination. Given what we know about the toxicity of these substances and the levels at which they are reported to occur, it is unlikely that they pose any risk to human health.

In our ongoing study of the quality of Great Lakes drinking water, we prepared toxicity profiles for a group of substances identified as possible candidates for further examination. For most of these substances, some data existed which could be used to develop a tentative toxicological assessment. However, analytical data for Great Lakes drinking water are lacking in the majority of cases and it is thus not possible to conduct a complete human risk assessment. It is interesting to note that, for those chemicals for which food residue data existed, exposure from drinking water was a lot less than that for food. Furthermore, current exposure levels to these substances are generally orders of magnitude lower than those required to induce minimal toxic effects in animals and are below equivalent tolerances have been established for these substances in food either by national or international authorities. I must cautiously point out however, that the toxicology data base for many of these substances in incomplete and additional studies of a chronic nature, along with reliable monitoring data on levels in water are required before any definite conclusions can be drawn.

While discussing the role of toxicology in the establishment of water quality objectives, it is important to recognize, as has been pointed out by countless others, that the standard setting process tends to treat chemicals individually. The possible combined effects of chemicals in drinking water or human health is not generally considered. In the report by the Toronto Board of Health attention is drawn to this fact. The authors of this report found no association between water mutagenicity index and cancer mortality rates in Ontario. A weak statistical correlation was observed between mutagenicity index and infant mortality in Ontario but no causal association was established and other confounding factors may have been responsible for this apparent outcome. In other jurisdictions the mutagenicity of water has been examined in more detail than here in Ontario. One of the most significant studies was recently published by a Dutch group who administered the concentrated mutagenic fraction of water to rats for their lifetime at 7, 22 or 68 times the equivalent human exposure level. Under the conditions of this test, it was concluded that the mutagenic impurities did not induce any tumors. This result is consistent with the data reported for cancer mortality by the Toronto Board of Health. The Dutch study, however, opens some exciting possibilities for future studies and I would encourage researchers to examine this approach in terms of its application in the Canadian setting.

While I spoke a few moments ago regarding the limitations of epidemiological studies it is nonetheless instructive to review what is known about such studies as they relate to drinking water. There are few studies available concerning the association between drinking water and human health effects and essentially no data exist in regard to this relationship for Great Lakes drinking water. The available epidemiological studies were conducted primarily in the United States and concerned water bodies such as the Ohio River basin, the Mississippi River and certain ground waters. It is instructive to comment on the data from these investigation areas because it may assist in defining the nature of studies required in future investigations of the health effects of Great Lakes drinking water.

The US studies are of two types, ecological and case-control studies. The available ecological studies, which are hypothesis generating studies in nature, suggest an association between consumption of surface water and cancer of the gastrointestinal tract. Case-control studies suggest an increased risk of rectal cancer, ranging from 1.13 to 1.93, in consumers of chlorinated versus unchlorinated water. In some studies, an increased risk of colon and bladder cancer was noted as well. In general, the observed increases are large enough to be of concern but small enough that they cannot be separated from confounding factors such as occupation, other forms of exposure to carcinogens, smoking, dietary habits and lifestyle. In addition, there are no positive dose-response data relating increasing exposure with increasing health effects. In particular, no data are available which associate specific drinking water contaminants or the total organic contaminant load with increased cancer risk. In summary, no causal relationship between drinking water exposure and increased cancer incidence has been found to date. It is possible, with improved experimental designs and access to high quality analytical data on retrospective contaminant levels, that more meaningful data may be generated, however, it must be pointed out that the increased risks lie, in all probability, near the limit of detection for epidemiological methods. To detect any increased risk to health associated with drinking water will require exquisite attention to methodological details in study design and analysis.

While not concerned specifically with drinking water, a recently reported Canadian study describes an increase in standardized mortality ratio (SMR) for all cancer sites in both males and females, and an increase in SMR's for liver and lung of female residents of Niagara County, Ontario. The authors noted that, because of the nature of the study, no conclusions could be drawn with respect to cancer incidence and drinking water and noted that the increased SMR's reported could have been due to confounding factors.

In another study designed to assess the effects on the newborn of heavy maternal consumption of PCB-contaminated Lake Michigan fish, reported behavioural defects in children born to these mothers as compared to controls who did not eat Lake Michigan fish. Because the observed effects did not correlate with umbilical cord PCB levels, the authors suggested additional investigations be conducted to further explore the causal relationships. In an extension of this study, behavioural parameters in the control group, who lived in communities adjacent to the lake, were compared to a second control group who lived in inland Michigan. No differences in behavioural outcomes were noted in the offspring of mothers from these two areas, suggesting that drinking water did not contribute to the behavioural problems.

The available epidemiological studies do not suggest that drinking water contributes significantly to human cancer risk. While certain studies conducted on populations which obtained drinking water from sources other than the Great Lakes produced results consistent with a slight increased risk for tumours of the gastrointestinal tract and bladder, no causal association has been established and confounding factors may account, in total or in part, for the observed increases. Special note should be made however of ongoing activities to develop comprehensive cancer registries in jurisdictions surrounding the Great Lakes which may assist in assessing increased risk associated with drinking water.

Future Directions

Let me turn for a moment to an examination of knowledge gaps and future directions necessary to ensure the safety and quality of Great Lakes drinking water. The Committee on the Assessment of Human Health Effects of Great Lakes Water Quality has pointed out that there are approximately 200 chemicals known to exist in the Great Lakes and for which there are insufficient data upon which to base a human risk assessment. As you have seen from my presentation, guidelines have been established for only a few substances. Is it necessary to establish guidelines for each and every one of these substances? I think not. What is required is a critical examination of these additional substances based upon their physical/chemical properties and existing toxicology data coupled with the toxicology of structurally analogous compounds and what information exist with regard to exposure levels in order to establish priorities for future action. While it is clear that detailed toxicological data bases will be required for some of these substances they certainly will not be required for all. For those priority substances selected it will be essential to begin to obtain good routine monitoring data to facilitate the risk assessment process. Given the fact that so few instances exist in which current guidelines are exceeded is it not time to think about a redistribution of resources to the newer more challenging problems?

Efforts must obviously continue to evaluate the potential health significance of combinations of chemicals in drinking water. Two approaches need to be considered here. Firstly it is suggested that efforts be expanded to develop new methodology to assess their potential effects in laboratory studies. Of paramount importance is the need to supplement the existing data base on the mutagenicity of water extracts with data in whole animal systems which will permit a more realistic appraisal of the health implications of the existing data. Secondly, support needs to be given to efforts of the International Joint Commission and others in the elucidation of appropriate epidemiological methods to evaluate the quality of existing water supplies.

In summary, it can be stated that Great Lakes drinking water generally meets existing national and international criteria for quality. However, it is not a time for complacency and much remains to be done.

Efforts to improve drinking water quality need to continue on two fronts, namely, intensified programs to clean up local hot-spots and expansion and broadening of existing monitoring and risk assessment activities with particular emphasis on newly detected organic substances.

TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER

John N. Hilton and Robert Machacek
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Key words: Water Treatment, Trace Organics, Drinking Water, Granular Activated Carbon, Great Lakes, Contaminant Removal.

ABSTRACT

More than 4 million Ontario residents rely on the Great Lakes as a source of drinking water. These surface bodies continue to be contaminated with organic chemicals of industrial and municipal origin, with over 200 man-made chemicals being identified recently in the Niagara River alone. Granular activated carbon is capable of removing many of these chemicals from drinking water supplies.

A pilot plant consisting of conventional water treatment processes plus granular activated carbon (GAC) adsorption contactors is being built to study the effectiveness of both conventional and GAC processes at removing trace levels of selected organic contaminants from drinking water. The pilot plant is located at the Niagara Falls Water Treatment Plant in Chippawa.

The removal of 35 organic compounds will be monitored at natural and at spiked influent levels. These compounds include: aromatics, halogenated aliphatics, chlorinated benzene derivatives, PCBs, organochlorine pesticides and herbicides, phenols, phthalates, polyaromatic hyrdocarbons, alkanes, alcohols, aldehydes, ketones and esters. Since these compounds are at trace levels, special methods have been developed for sampling, concentrating and analyzing water containing this mixture of chemicals at nanogram pe

TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER

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INTRODUCTION

This project is designed to investigate the removal of trace organic compounds from Great Lakes water which is used as a drinking water supply by more than 4 million Ontario residents.

The specific objectives of the project are:

1. to assess the effectiveness of both optimized conventional drinking water treatment and activated carbon adsorption (add-on contactor mode) for the removal of trace organic contaminants.

2. to determine process operational parameters for both systems.

At the present time Ontario drinking water meets Drinking Water Objectives. However, given the continual influx of organic compounds into the Great Lakes, the potential exists for future problems. In addition, there is an ongoing effort toward analysing for a larger number of organic compounds and obtaining lower detection limits.

Various government agencies on both sides of the Canada-U.S. border are working to provide drinking water guidelines for organic chemicals commonly found or anticipated in raw and finished waters. In fact, the U.S. EPA has recently proposed drinking water standards for 32 synthetic organic chemicals, including proposed limits for several pesticides and PCB's, of zero mg/L. These standards are based on effective water treatment methods now available, such as filtration through granular activated carbon.

A pilot plant is presently being built for use at the Niagara Falls Water Treatment Plant in Chippawa. Early on-site work will focus on optimizing organics removal in the conventional water treatment process by evaluating the performance of various coagulant chemicals and coagulant aids. After the most effective combination of chemicals and dosages has been determined, the entire treatment train including GAC adsorption contactors will be used over a 12 month period at essentially steady state conditions. Predictive modelling will be used to estimate the breakthrough of some of the 32 target compounds that have been selected to monitor the performance of the GAC contactors. A complex spiking program will be undertaken to provide steady influent concentrations of some of the target compounds not detected in the raw water in order to test the full capabilities of carbon over a wide range of organic compound groupings.

Sampling schedules and analytical procedures will ge geared to measuring actual contaminant breakthroughs in the GAC column, as predicted by the pore surface diffusion model (PSDM).

SELECTION OF TARGET COMPOUNDS

The initial selection process for target compounds to be monitored during the pilot plant operation began with a list of over 300 organic chemicals that have been found in the Great Lakes ecosystem. This list was compiled from several different references, including works by the International Joint Commission (IJC), the Niagara River Toxics Committee (NRTC), the Ontario Ministry of the Environment (MOE), the New York Public Interest Research Group (NYPIRG) and the City of Toronto Department of Public Health and Department of Works.

The following information was gathered for each chemical:

Identification

Chemical Name
CAS - Chemical Abstracts Service Registry Number

Environmental Levels

The frequency and maximum amount detected in the Niagara Falls water treatment plant raw water by routine, bi-weekly MOE monitoring of organics.

Physical, Chemical and Toxicological Properties

Henry's Law Constant
Aqueous Solubility
log K_{ow}
Complexation Potential with TOC
Liquid Phase Diffusion Coefficient
Activated Carbon Capacity
Bioconcentration Factor
LC_{50}
LD_{50}
NRTC Hazard Class Rating

Aquatic and Drinking Water Criteria

Ministry of the Environment
U.S. Environmental Protection Agency
World Health Organization

The initial screen of all the chemicals found in the Great Lakes ecosystem was based on the availability of quantitative environmental and toxicological data. Compounds without much data available were given little further consideration. The second screen for chemicals with quantitative data was based mainly on the Categories of Concern developed by the Niagara River Toxics Committee. One of the principal tasks of the NRTC was to assess the sigificance of the types and levels of chemicals found in the Niagara River. The screening methodology involved in establishing a priority ranking involved three major types of information. Criteria information was taken from several agencies and included criteria for the protection of aquatic life, human health, etc. Chemical and toxicological information included bioaccumulation and accute toxicity data, and other health parameters considered in various other toxicity scoring methodologies. Environmental occurrence information was compiled from responsible jurisdictions, involved in the Niagara River Toxics Project. The screening process resulting in three major groups and several subgroups of chemicals, of which group I, and groups IIA and IIB chemicals are considered to be of most concern. This is based on concentrations of these chemicals identified in the Niagara River with respect to levels at which they are considered to pose risks to human health and/or environment. Designation as an EPA priority pollutant was also considered in the screening process.

Chemicals listed as NRTC group I, IIA or IIB compounds or as EPA priority pollutants were screened again to determine if they were present in the raw water supply at the Niagara Falls Water Treatment Plant. This was accomplished by reviewing MOE routine, biweekly monitoring of several classes or organic compounds in the Niagara raw water over a period of two years. This was done to help establish sampling and spiking needs in the overall experimental plan.

Compounds not passing previous screens were then considered against other compounds in the same chemical class (eg., pesticides, phthalates, polyaromatic hydrocarbons). An attempt was made to have a complete range of high to low values of chemical and physical properties that affect organic chemical removal processes represented within each chemical class. For example, Henry's Law Constants provide an indication of the ability of a chemical to be removed by aeration or air stripping processes. Compounds that were felt to contribute to the overall range of properties within their class were considered further.

The final acceptance criteria was based on practical considerations for the spiking, sampling and analytical programs. Chemicals that presented problems were rejected. For example, compounds for which acceptably low detection limits could not be achieved were excluded. Another example is the dioxin 2,3,7,8-TCDD. Although this is a compound of tremendous concern, the problems with spiking, sampling and shipping samples containing dioxin are obvious. The selection process is shown in a flowsheet form in Figure 1.

The total number of target compounds is limited by budget constraints, as analytical costs for regular monitoring of

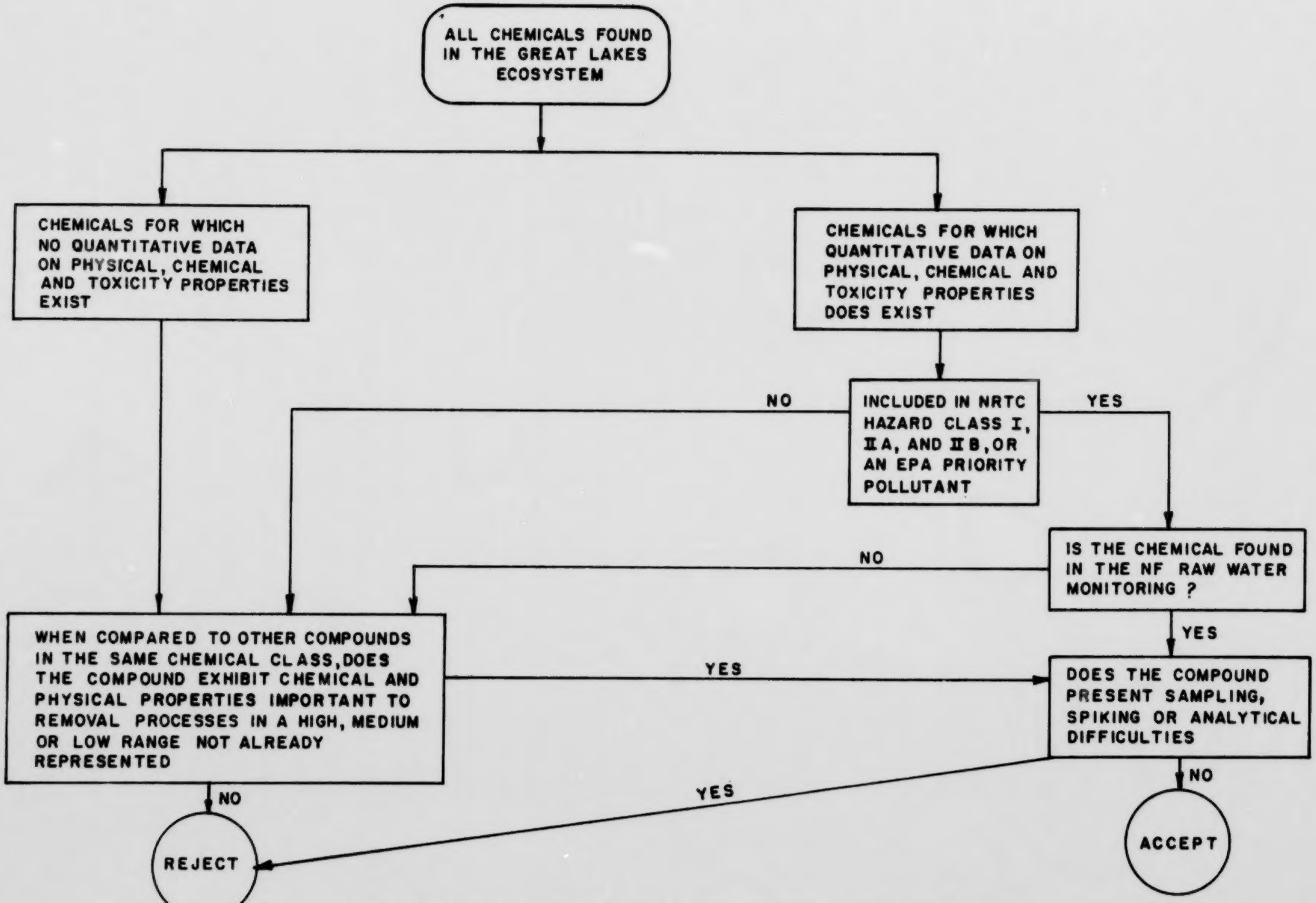
ALL CHEMICALS FOUND IN THE GREAT LAKES ECOSYSTEM
CHEMICALS FOR WHICH NO QUANTITATIVE DATA ON PHYSICAL, CHEMICAL AND TOXICITY PROPERTIES EXIST
CHEMICALS FOR WHICH QUANTITATIVE DATA ON PHYSICAL, CHEMICAL AND TOXICITY PROPERTIES DOES EXIST
NO
INCLUDED IN NRTC HAZARD CLASS I, II A, AND II B, OR AN EPA PRIORITY POLLUTANT
YES
NO
IS THE CHEMICAL FOUND IN THE NF RAW WATER MONITORING ?
YES
WHEN COMPARED TO OTHER COMPOUNDS IN THE SAME CHEMICAL CLASS, DOES THE COMPOUND EXHIBIT CHEMICAL AND PHYSICAL PROPERTIES IMPORTANT TO REMOVAL PROCESSES IN A HIGH, MEDIUM OR LOW RANGE NOT ALREADY REPRESENTED
YES
DOES THE COMPOUND PRESENT SAMPLING, SPIKING OR ANALYTICAL DIFFICULTIES
NO
YES
NO
REJECT
ACCEPT

FIGURE I. SELECTION PROCESS FOR TARGET COMPOUNDS

over 30 organic compounds are quite large. The list of target compounds chosen is shown in Table 1.

ANALYTICAL PROTOCOLS

The analytical protocols center around various methods of analysis of different sample fractions. These fractions include the volatile organics fraction obtained by the purge and trap extraction methods, and the base/neutrals acid, pesticides, PAHs and chlorinated phenols/herbicides fractions, which are obtained through high volume liquid/liquid extraction methods.

The establishment of the final analytical protocol is still in progress. Once these protocols are established, the process of validating method detection limits, precision and accuracy will be repeated.

The following presents the general framework of the methods involved, along with approximate, expected detection limits. Compounds in parentheses have lower detection limits when a different method of analysis is used.

Volatile Organic Analysis

The volatile organic analysis (VOA) is used to determine compounds which have a high vapour pressure and low water solubility, and can therefore be purged from water into a gas stream. These compounds include most of the commonly used organic solvents and degreasers. The compounds are stripped from water using a modified purging device and detected using a Gas Chromatograph/Mass Spectrometer (GCMS).

For the analysis, one litre of sample is placed in the stripping vessel and purged with a stream of helium for 30

TABLE 1

LIST OF TARGET COMPOUNDS

Chemical Class	Compounds
Halogenated Aliphatics	Chloroform Carbon tetrachloride 1,2-dichloroethane Hexachlorobutadiene Tetrachloroethylene
Aromatics	Benzene o-Xylene
Chlorinated Benzene	Chlorobenzene 1,4-dichlorobenzene Hexachlorobenzene 1,2,4-trichlorobenzene
Organochlorine Pesticides	alpha-BHC p,p'-DDT Heptachlor epoxide
Phthalates	di-n-butylphthalate bis (2-ethylhexyl) phthalate
Phenols	Phenol 2,4,6-trichlorophenol Pentachlorophenol
PAH's and Related Compounds	Anthracene Benzo(a)pyrene Naphthalene Pyrene
Alcohols/Ketones/ Esters/Aldehydes	2-butanone 1-decanol Isobutanol Hexanal Methyl hexadecanoate
Alkanes	Decane Hexadecane Hexane
Herbicides	2,4-D

minutes. Eighty grams of sodium sulfate is added to the sample to increase the stripability of the higher vapour pressure compounds. The purged compounds are adsorbed onto a gel trap at 25 C. After purging is completed, the trap is heated to 180 C and flushed with the helium carrier gas into the GC capillary column. As the organics desorb from the trap, they are concentrated at the front end of the capillary using a liquid nitrogen cryogenic trap. After the desorption is complete (2.5 min) the GC oven is temperature programmed and the compounds are detected by the mass spectrometer as they elute from the GC column. The compounds are identified using retention time and verified by the mass spectrum of the compounds. The following compounds will be analysed using this method:

COMPOUND	DETECTION LIMIT (ng/L)
Halogenated Aliphatics	
Chloroform	10
Carbon Tetrachloride	5
1,2-Dichloroethane	5
Tetrachloroethene	5
(Hexachlorobutadiene)	50
Aromatics	
Benzene	20
o-Xylene	10
Chlorinated Benzenes	
Chlorobenzene	5
1,4-Dichlorobenzene	5
(1,2,4-Trichlorobenzene)	10

PAH's	
(Naphthalene)	5
Alcohols/Ketones/Esters/Aldehydes	
2-Butanone	10
Isobutanol	50
Hexanal	10
(1-Decanol)	50
Alkanes	
Hexane	5
(Decane)	50

High Volume Liquid-Liquid Extractions

In order to increase the sensitivity of the analytical methods requiring liquid-liquid extractions (LLE) it was decided to increase the volume of water extracted from one litre to 16 litres. Because of the difficulty of extracting sixteen litres of water at one time, the high volume LLE (HVLLE) consists of combining the extracts from 4 four litre extractions. The four litres of water to be extracted are adjusted to pH 12 with NaOH. The water is then extracted three times with 150 ml of methylene chloride. The combined basic extract is dried over anhydrous sodium sulfate and concentrated. The water is then adjusted to pH 2 with HCl and again extracted three times with 150 ml methylene chloride. The combined acid extract is dried over anhydrous sodium sulfate and concentrated.

The (HVLLE) analysis actually consists of four different analyses on the same extract. The basic extract can be used for the GCMS BN analysis, the polynuclear aromatics analysis, and chlorinated pesticides analysis. The acid extract can be used for the GCMS Acid analysis and the chlorinated phenols by GC/ECD analysis.

Base/Neutral/Acid Fraction by GCMS

The Base/Neutral/Acid (BNS) fractions are injected into the GCMS. The compounds are identified using retention time and verified using mass spectra.

The following compounds will be analysed using this method:

COMPOUND	DETECTION LIMIT (ng/L)
Chlorinated Benzenes	
(1,4-Dichlorobenzene)	5
1,2,4-Trichlorobenzene	10
Hexachlorobenzene	10
Halogenated Aliphatics	
Hexachlorobutadiene	50
Phthalates	
Di-n-butylphthalate	20
bis(2-Ethylhexyl)phthalate	20

Phenols	
Phenol	50
(2,4,6-Trichlorophenol)	50
(Pentachlorophenol)	100
PAH's	
(Anthracene)	20
(Benzo(a)pyrene)	20
(Naphthalene)	5
(Pyrene)	20
Alcohols/Ketones/Aldehydes	
1-Decanol	20
Methylhexadecanoate	20
Alkanes	
Decane	10
Hexadecane	20

High Volume Pesticides

The base/neutral fraction of the high volume extraction can be analysed using a GC with electron capture detector (GC/ECD). This will determine the organochlorine pesticides. The methylene chloride extract would be transferred to hexane and concentrated to 5 ml. This hexane extract would be analysed by GC. The compounds would be identified based on retention time on two different capillary columns.

The following compounds will be analysed using this method:

COMPOUND	DETECTION LIMIT (ng/L)
alpha-BHC	0.5
p,p'-DDT	0.5
Heptachlor epoxide	0.5

High Volume Polynuclear Aromatic Hydrocarbons

The Base/Neutral fraction of the HVLLE can also be analysed by High Pressure Liquid Chromatography (HPLC) for the Polynuclear Aromatic Hydrocarbons (PAH). The extract would be injected into a HPLC. The compounds would be identified using both retention time and ratio of the fluorescence and ultra-violet detector responses.

The compounds detected with this method are as follows:

COMPOUND	DETECTION LIMIT (ng/L)
Anthracene	0.1
Benzo(a)pyrene	0.1
Naphthalene	0.1
Pyrene	0.1

Chlorinated Phenols/Herbicides

The fraction is injected into a GC/ECD. The compounds are identified using retention times.

The following compounds are detected in these fractions:

COMPOUND	DETECTION LIMIT (ng/L)
Herbicides	
2,4-D	10
Chlorinated phenols	
2,4,6-Trichlorophenol	1
Pentachlorophenol	5

PILOT PLANT DESIGN

General Configuration and Materials of Construction

The pilot plant will model a complete water treatment process consisting of flash mixing and coagulation, flocculation, sedimentation and filtration, followed by granular activated carbon adsorption. A single treatment train is provided through filtration. After filtration there are four parallel adsorption process trains, 2 of which serve as backup, ie., each process train is replicated once.

The first process train consists of a single adsorption vessel with a 20 minute empty bed contact time (EBCT). The second process train has three adsorption beds operating in series with EBCT of 1 minute, 9 minutes and 10 minutes each respectively.

The materials of construction as well as process equipment and instrumentation have been carefully selected so that all water-contacting surfaces throughout the entire delivery and treatment processes are of chemically inert substances (i.e., glass, teflon and stainless steel). The design criteria for the various unit processes are described below.

Raw Water Supply

The pilot plant is supplied with raw water from the Niagara River through the Niagara Falls Water Treatment Plant's intake system. The draw-off point is in the influent conduit after the travelling screens, but prior to the low lift suction well and the prechlorination and powdered activated carbon addition points. A dedicated stainless steel pump and supply line deliver raw water to the pilot plant, located in the low lift pumping station.

Flash Mixing

Flash mixing for both the addition of coagulants, filter-aid and organic spiking compounds is done with an 8 stage Komax-type static mixer.

Flocculation

The flocculator is designed for a 3.8 L/min (1 U.S. gpm) flow. It is divided into 3 compartments, each of which has a hydraulic detention time of 10 minutes. Each compartment has an individually controlled stirrer capable of producing an energy input in the range of $G = 5$ to 30 sec^{-1}.

Sedimentation

The sedimentation process occurs in a lamella clarifier. The lamella plates are 244 cm (8 ft) long and are inclined at an angle of 55° to the horizontal. The plate separation

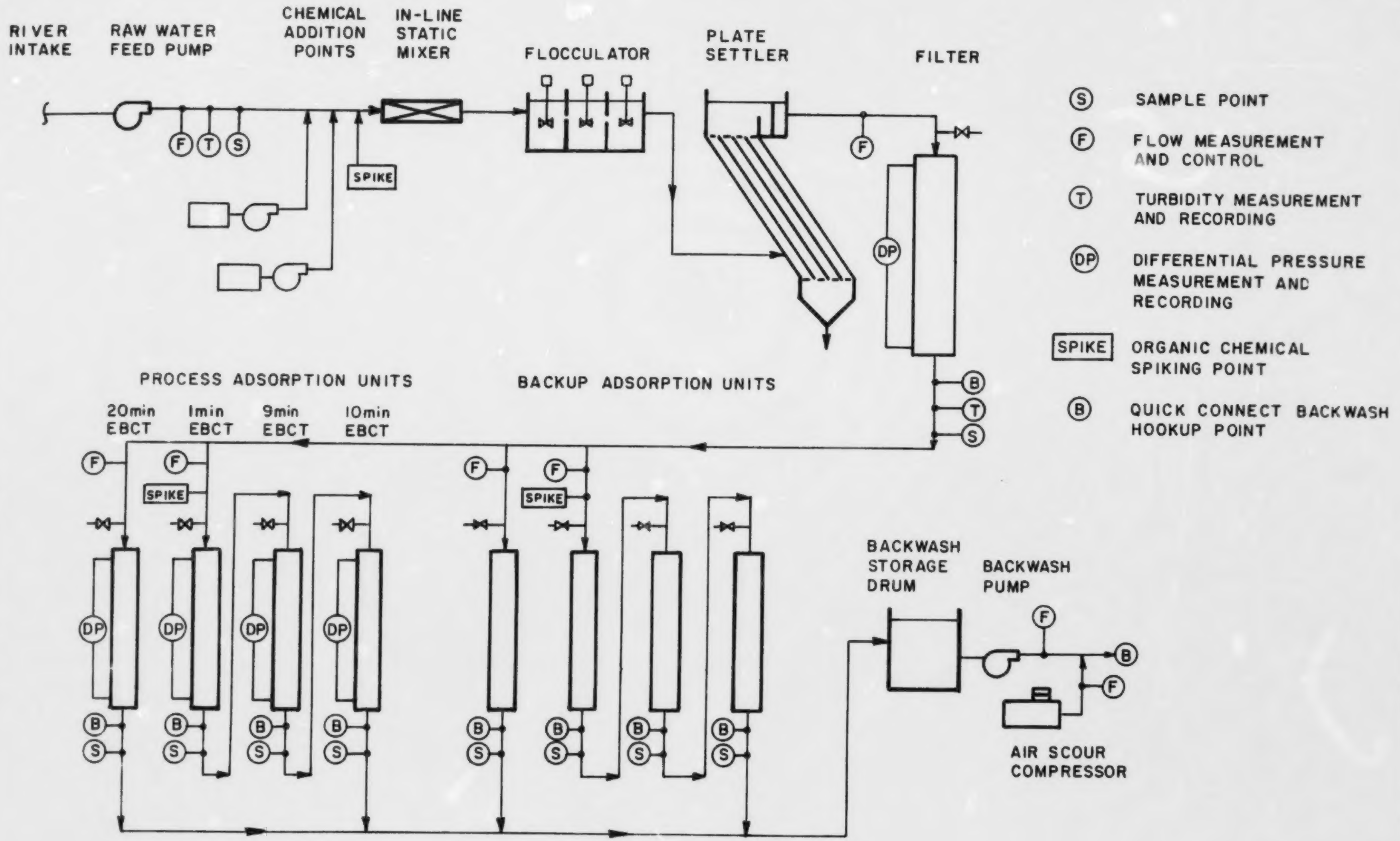
RIVER INTAKE
RAW WATER FEED PUMP
CHEMICAL ADDITION POINTS
IN-LINE STATIC MIXER
FLOCCULATOR
PLATE SETTLER
FILTER
F
T
S
SPIKE
DP
B
PROCESS ADSORPTION UNITS
20min EBCT
1min EBCT
9min EBCT
10min EBCT
BACKUP ADSORPTION UNITS
BACKWASH STORAGE DRUM
BACKWASH PUMP
AIR SCOUR COMPRESSOR
S SAMPLE POINT
F FLOW MEASUREMENT AND CONTROL
T TURBIDITY MEASUREMENT AND RECORDING
DP DIFFERENTIAL PRESSURE MEASUREMENT AND RECORDING
SPIKE ORGANIC CHEMICAL SPIKING POINT
B QUICK CONNECT BACKWASH HOOKUP POINT

FIGURE 2. SIMPLIFIED PROCESS FLOWSHEET

is 5.1 cm (2 inches) and plate width is approximately 23.5 (9¼ inches). The overflow rate of the lamella clarifier is 115,709 L/d/m^2 (2,840 gpd/ft^2).

Filtration

The filter is a 10.2 cm (4 inch) diameter column, 305 cm (10 feet) high. It is constructed from glass pipe and capped with 304 stainless steel flanges. The lower flange has a built-in plenum with a flow divider plate and stainless steel media retainer. The filter will operate at a flowrate of 204 L/d/m^2 (5 gpm ft^2).

Carbon Adsorption

The carbon adsorption contact vessels are constructed exactly as the filter with the exception that they are 7.6 cm (3 inches) in diameter. At the empty bed contact times stated above, the flow rate through each adsorption train is 0.237 L/min (0.0625 U.S. gpm).

Instrumentation

A recording turbidimeter is installed at two points in the pilot plant. These are at the entrance point for the raw water and at the filter effluent. Filter head loss is measured by a differential pressure (DP) cell. There are also DP cells on four of the eight carbon adsorption vessels. As with the turbidimeters, the DP cells are outfitted with strip chart recorders.

Organic Spiking Points

Spiking points for organic chemicals are located at the entrance to the flocculator and in the filter effluent, upstream of the two carbon adsorption process trains which consist of the three adsorption vessels in series.

Sampling Points

Sample valves in the pilot plant are located on the raw water supply, the filter effluent and at the end of each carbon adsorption vessel. In addition, samples may be taken from the free water surfaces in the flocculator and the sedimentation tank.

Concluding Remarks

At the time of writing, the pilot plant equipment has been delivered and will be assembled on site by January 1986. It is anticipated that the test program will begin by the end of January.

PILOT TESTING PROGRAM FOR POTABLE WATER TREATMENT FOR COLOURED NORTHERN ONTARIO WATER

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M.M. Dillon Ltd.

Key words: Water Treatment, Colour Removal, Ozonation, Northern Ontario, Atikokan River.

ABSTRACT

This paper describes pilot testing of colour removal processes for raw water from the Atikokan River. Processes used during the testing program, which ran from Summer 1984 to Spring 1985, include:

- ozonation;
- ozonation followed by granular activated carbon adsorption;
- ozonation followed by alum coagulation and dual media filtration;
- alum coagulation and dual media filtration.

Ozone dosages up to 8 mg/L, combined with ozone contact times ranging from 2 to 20 minutes, reduced organic colour by approximately 50 per cent. Even at 8 mg/L ozone dosage, disinfection was not complete.

EBCTs ranging from less than one minute to over one hour were used in evaluating granular activated carbon (GAC). Increases in effluent SPC indicate biological growth on the GAC. No biological regeneration of the GAC was noted under the test conditions. Colour removal on GAC ceased before 7,000 bed volumes of water were treated.

Parallel direct filtration runs show that less coagulation (alum and polymer) are required when the water is pre-ozonated.

The alternative colour removal processes are evaluated on the basis of operating cost (at Atikokan) for colour removal to 5 H.U. The secondary consideration, reduction of trihalomethane formation potential to less than 350 mg/L, is met by all processes reducing organic colour to less than 5 H.U.

Process design for a new Potable Water Treatment Plant for the Township of Atikokan, using pilot testing results, is discussed.

PILOT TESTING
FOR
ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER AT ATIKOKAN, ONTARIO

BY

T. A. Constantine, P. Eng.
K. Sakamoto, P. Eng.
G. W. Lai

I. INTRODUCTION

OBJECTIVES OF THE STUDY

This study was funded by the Ontario Ministry of the Environment Research Advisory Committee to pilot-test processes to remove organic colour and trihalomethane (THM) precursors from northern waters.

The study was continued through the year to test the processes under all conditions of temperature and water quality.
The Township of Atikokan was used for pilot testing.

RAW WATER QUALITY

Potable water for Atikokan is taken from the Atikokan River at Little Falls. The water used in pilot testing is taken from the intake pipe.

Raw water quality is presented in Table 1.

TABLE 1

ATIKOKAN PILOT TESTING
RAW WATER QUALITY

Parameter	September	November	February	May
Colour - HU	39	35	22	40*
Turbidity - NTU	0.84	1.5	0.7	0.9
Hardness - mg/L $CaCO_3$	30	30	-	25
Alkalinity - mg/L $CaCO_3$	25	24	22	15
pH - pH Units	7.3	7.4	6.3	6.9
Iron - mg/L Fe	0.20	0.25	0.25	0.3
Manganese - mg/L Mn	0.015	0.011	-	0.026
Conductivity - umho/cm	62	66	-	60
Temperature - Degrees C	15	1.5	0	15
Total THM Potential - ug/L	460	890	-	-
Dissolved Organic Carbon - mg/L	7.2	9.8	8.2	10.8

*Note: Maximum 76 HU.

LITERATURE REVIEW

Organic Colour

The characteristic yellow-orange colour of many northern surface waters is due to the presence of humic substances. Humic substances are recognized as precursors of trihalomethane.

Humic substances originate from decay of plant matter and:

- are not readily biodegradable (7)
- are complex hydrophilic, predominantly aromatic anionic polyelectrolytes containing the following function groups:
- carboxyl (-COOH)
- methoxyl ($-OCH_3$)

- phenolic and alcoholic hydroxyl ($-OH$)

- ketone ($-C=O$)

- exhibit "acid-base indicator" action. Colour increases with pH

- have a particle size range for 3.5 to 10 nm diameter.

Humic substances are classed according to their solubilities:

	Acid	Alkali	Alcohol
Fulvic Acid	Soluble	Soluble	
Humic Acid	Insoluble	Soluble	Insoluble
Hymatomelanic Acid	Insoluble	Soluble	Soluble

Many investigators do not distinguish between humic and hymatomelanic acids (3).

Coloured water from various surface water sources were uniform in percentage content of each class of humic material (1,3,5,7):

- 87% fulvic acid
- 2% humic acid
- 11% hymatomelanic acid.

Characteristics of fulvic and humic acids are presented below:

	Fulvic Acids	Humic Acids
Molecular Weight (9)	300 - 3 000	5 000 - 100 000
Ultimate Analysis (3)		
- C	40 - 50%	50 - 60%
- H	4 - 6%	4 - 6%
- O	44 - 50%	30 - 35%
- N	L 1 - 3%	2 - 6%
- S	0 - 2%	0 - 2%
Colour of 1 mg/L Solution (1)	2.8 H.U.	26.5 H.U.

Coagulation of Organic Colour

Babcock and Singer (2) conclude that "Coagulation of humic and fulvic acids by alum causes color and TOC reductions that result in the production of less chloroform upon chlorination."

Hall and Packham (11) found a stoichiometric relation between optimum coagulant dosage and raw water colour. Data from MOE water treatment plants (12) shows average alum dosages of 1 mg/L per Hazen Unit of colour.

Coagulation with alum produces insoluble aluminum humates and fulvates (3) by interaction between positively charged hydrolysed aluminum and carboxyl groups on the humic molecule.

Optimum pH for alum coagulation is pH 5-6 (3).

Operational parameters for organics removal are summarized in the AWWA Committee Report (3) as follows:

- Rapid Mix Time: Neither the speed of addition of the flocculant nor the method and time of mixing has a significant impact on humic acid removal.

- Flocculation Time: Some benefit may be obtained by extending flocculation time.

- Order of Addition: The sequence of chemical addition affects colour removal and varies for different waters.
- Coagulant Type: Both alum and iron salts are effective in removing humic and fulvic acids from water. High molecular weight polymers should be added after alum in order to bridge the destabilized floc particles.
- Coagulant Dosages: Dosages are proportional to the concentration of humic and fulvic acids. Dosages decrease with decreasing pH.
- pH Correction and Stabilization: Best stabilization may be achieved by chemical addition after sedimentation but before filtration.

Preozonation is reported to improve removal of organics by coagulation (14, 23, 24).

Activated Carbon

Activated carbon has been used in the past in potable water treatment for taste and odour control. Activated carbon removes organics from the water by adsorption. Factors affecting adsorption (10) include:

- physical and chemical characteristics of the activated carbon (e.g. surface area, pore size, chemical functional groups)
- physical and chemical characteristics of the organics (e.g. size of molecule, polarity, chemical functional groups)
- concentration of organics in the water

- characteristics of the water (e.g. pH, temperature, ionic strength)

- contact time between water and carbon in the system.

Activated carbon has been found to have only limited effectiveness in removing naturally occurring organics from water (3, 21).

Adsorption isotherms, relating the distribution of adsorbate between the adsorbed phase and the solution phase can be used to determine theoretical adsorption capacity. The Freundlich isotherm describes one such relationship. The Freundlich isotherm describes one such relationship. The Freundlich equation is:

$$\frac{x}{m} = KC^{1/n}$$

where x = amount of adsorbate adsorbed
m = mass of carbon
C = equilibrium concentration of adsorbate in solution after adsorption
K = constant related to adsorption capacity, i.e., the mass of adsorbate adsorbed per unit mass of carbon
$1/n$ = constant related to adsorption intensity.

Typical values of the Freundlich constant for Calgon F400 carbon are:

Humic Substance	Freundlich Constant K	Freundlich Constant 1/n	Reference
Soil Humic Acid	20.5	0.508	30
Commercial Humic Acid	1.905	1.818	21
Commercial Humic Acid	25	0.678	30
Peat Fulvic Acid	5.282	0.519	21
Peat Fulvic Acid			
- MW L 1 000	31.136	0.610	21
- MW G 50 000	4.163	0.555	21
Soil Fulvic Acid	8.2	0.206	30
Leaf Fulvic Acid	35	0.534	30

Lee, et al. (21) conclude, however, that actual carbon bed service life cannot be predicted on the basis of equilibrium capacity or phenol number or surface area (BET).

The literature (22, 24, 25, 26, 27, 28, 29, 8) describes full scale water treatment plants with GAC beds with extended life (design bed life of 100 000 BV (25)). Extended bed life is attributed to biological degradation of adsorbed organics, that is biological regeneration. These carbon filters have been called "biologically active filter" or BAF.

The effectiveness of biological regeneration depends on the biodegradability of the adsorbed organics (19, 31). Humic substances are not biodegradable. European experience (loc. cit.) indicates preozonation is necessary to produce easily biodegraded organics and to supply sufficient oxygen to permit efficient operation of a BAF bed. When a new BAF bed is put into service, initial removal of organics is high. The high removal is attributed to adsorption. After the initial operating period and prior to bed saturation and adsorbate breakthrough, a "steady state" removal is reached, providing extended bed life. Biodegradable organics removal in this stage has been observed to be lower, in the order of 20-30% (3, 21, 27, 29,33).

Treatment Processes Tested

The pilot plant was set up to test the effect on colour removal of:

- ozonation
- alum coagulation
- granular activated carbon adsorption
- biologically active carbon filters.

Ozonation as a separate unit process and as a pretreatment process was examined at various combinations of ozone dosage and ozone contact times.

Alum coagulation of colour was pilot tested using dual media direct filters (no sedimentation) on:

- preozonated water to evaluate the effect of ozone on alum coagulation and colour removal

- raw water to act as a control.

Granular activated carbon treatment of preozonated water was carried out to determine adsorptive bed life and biological regeneration of activated carbon in extended carbon column runs.

II. EQUIPMENT AND ANALYTICAL PROCEDURES

PILOT PLANT

The pilot plant comprises:

- 2 lb/day ozone generator (PCI Model G2), complete with air preparation system (air compressor, dust filter, automatic regenerating air dryer).
- 215 mm id x 4.57m glass ozone contact column with a porous metal diffuser.
- 150 mm diameter PVC filter columns.
- Self-priming centrifugal raw water pump capable of delivering a maximum of 1.5 L/s as installed.

The pilot plant is set up in the Little Falls Pump House as shown schematically in the appended Drawing.

Raw water is taken from a 20 mm sample tapping in the existing intake line. Static water level is approximately 1.5m above the pump house floor. Raw water flow rate is controlled by throttling and/or by- passing at the raw water sample line.

The ozone contact column is erected in the pipe gallery with the bottom of the column 1.8m below floor level. This was done to accommodate the 5.2m high column support frame in the pump house with a 4.3m ceiling height. Ozone contact time can be varied by changing the height of water in the column (limited adjustment) or by changing water flow rate. Ozonated water in excess of filter requirements is wasted through the by-pass/drain valve in the contact column discharge pipe.

The filter columns are 150 mm PVC pipe sections. Filter CF-2 (Stages 1 and 2) are 925 mm high; the remainder are 1.25m high. Each filter is equipped with a valved 13 mm filter effluent/backwash hose connection and a 32 mm ABS overflow pipe 115 mm below the top of the columns. The filter columns are backwashed with potable water. The following is a description of the filters.

Phase 1

a) Carbon Filters

CF-1: 215 mm of activated carbon (Calgon Filtersorb F400) over 150 mm of filter gravel (1/4 x 1/8)

CF-2, Stage 1: 315 mm of activated carbon (F-400) over 150 mm of filter gravel

CF-2, Stage 2: 420 mm of activated carbon (F-400) over 150 mm of filter gravel

b) Conventional Direct Filter

DF-1: 230 mm of anthracite filter media (0.80 to 1.0 mm) and 230 mm of filter sand (0.45 to 0.55 mm) over 150 mm of filter gravel

c) Ozonated Direct Filters

OF-1: Media depths as for DF-1

OF-2: Media depths as for DF-1

Phase 2

a) Carbon Filters

CF-1: Same bed as Phase 1 (old carbon)

CF-2, Stage 1: Same bed as Phase 1 (old carbon)

CF-2, Stage 2: Same bed as Phase 1 (old carbon)

CF-3: 250 mm of activated carbon (F400) over 150 mm of filter gravel

b) Conventional Direct Filter

DF-1: Same filter as in Phase 1

c) Ozonated Direct Filters

OF-1: Same filter as in Phase 1

Phase 3

a) Carbon Filters

CF-1: (
CF-2 - Stage 1: (250 mm of new GAC (F400) over 150 mm of
CF-2 - Stage 2: (filter gravel
CF-3: (

b) Conventional Direct Filter

DF-1: As in Phases 1 and 2

c) Ozonated Direct Filter

OF-1: As in Phases 1 and 2

Phase 4

a) Carbon Filters

CF-1: Old GAC
CF-2: New GAC in both stages. Repiped to treat raw (unozonated) water.

b) Conventional Direct Filter

DF-1: Old media

c) Ozonated Direct Filters

OF-1: Old media (for comparison with CF-1)
OF-2 New media

Because the ozone contact column was lowered 1.8m into the pipe gallery, available head for gravity flow was reduced. Consequently, the filter columns were reduced in height from the originally planned 2.1m to 1.2m halving media depth. The low available head also necessitate siphon discharge from the filter columns.

Filter rates are measured by collecting filter effluents.

The chemical metering pump is a 4-head peristaltic pump. Ratios of chemicals fed are varied by changing pump heads and chemical solution concentrations. Dosages are changed by changing pump speed or solution strength.

Available range of flows and chemical dosages are:

-	Ozone generator	0 - 2 lb/d
-	Flow to ozone contactor	Up to 1.5 L/s
-	Ozone dosage range	Up to 7 mg/L at maximum water rate Up to 35 mg/L at low flow rate
-	Ozone contact time	2 min to 20 min
-	Filter rates	Up to 30 m/hr.

CHEMICALS AND FILTER MEDIA

Alum used was commercially available water treatment grade-powdered alum from Allied Chemicals.

The polyelectrolyte used was Dow Separan NP10, a non-ionic polymer.

The activated carbon was Calgon Filtersorb F400. Characteristics are:

-	BET surface area	1 100 m^2/g
-	Particle density	0.81 g/cm^2
-	Pore volume	0.7570 cm^3/g
-	Average pore diameter	27.5 Å
-	Effective size	0.65 mm

Uniformity coefficient	1.5

Anthracite filter media had the following characteristics:

Effective size	0.88 mm
Uniformity coefficient	1.6

The filter sand had the following characteristics:

Effective size	0.54 mm
Uniformity coefficient	1.4

FIELD ANALYSES

The objective of this study is to determine the effects of ozone and activated carbon or direct filtration on colour removal from a Northern water, typified by Atikokan's water.

Field analyses done were:

- Colour
- pH
- Alkalinity
- Hardness
- Temperature
- Ozone gas concentration
- Ozone residual in water
- Chlorine demand.

Apparent colour was determined with a spectrophotometer using the method described by Crowther and Evans ("Estimating Colour in Hazen Units by Spectrophotometry", Jour. AWWA 73: 265, May 1981). The instrument was calibrated against standard potassium chloroplatinate/cobaltous chloride solutions. The calibration curve was checked against a Hach colour comparator using raw and treated waters in Atikokan.

pH was measured using a Beckman Electromate pH Meter with a combination electrode.

Alkalinity (total) was determined by titrating a 500 mL aliquot with 0.020N sulphuric acid to a pH 5.1 end point.

Hardness was determined by titrating 250 mL aliquots with 0.1M EDTA solution using Eriochrome Black T as an indicator.

Ozone gas sample volumes (inlet gas and exhaust air) were measured using a wet gas test meter. The ozone was absorbed in a potassium iodine solution. The liberated iodine (in acid solution) was titrated with 0.005N sodium thiosulphate solution to a starch end point.

Ozone residual in the water was determined by the DPD method using a Hach chlorine residual comparator. The chlorine residual reading was multiplied by 0.68 to correct for the difference in molecular weights.

Chlorine demand was determined by adding sodium hypochlorite solution to 1L aliquots of raw water. Initial chlorine concentration was measured using the DPD method. After standing at room temperature for one hour in the dark, final chlorine residual was measured.

OTHER ANALYSES

The MOE laboratory in Toronto analysed water samples for:

- trihalomethane formation potential on samples dosed with 10 mg/L chlorine as sodium hypochlorite
- dissolved organic carbon (DOC).

The MOE Laboratory in Thunder Bay analysed water samples for:

a) Chemical and Physical Quality

- turbidity
- colour
- pH
- total alkalinity
- total hardness
- iron
- manganese.

b) Bacteriological Quality

- standard plate count
- total coliforms
- fecal coliforms
- fecal streptococci.

III. RESULTS OF PILOT TESTING

GENERAL

Analyses of the data are on the entire year's results, with water temperature being taken into account where applicable.

The filter columns, particularly those operating on ozonated water, were susceptible to air-binding. The filters were "bumped" using a 1/2 minute± backwash, hence filter run times could not be evaluated.

In the following discussion, the reference is to a raw water colour ranging from about 15 H.U. to 60 H.U. with an average colour of 35 H.U. and temperatures ranging from 0 to 20°C.

OZONE TRANSFER

Ozone transfer efficiency appeared unrelated to ozone dose, contact time or water temperature in this test.

Ozone transfer data are presented in Table II below:

TABLE II

OZONE TRANSFER EFFICIENCY

Water Temperature °C	Ozone Dose mg/L	Contact Time Minutes	Transfer Efficiency Per Cent
15	4.7	2.9	85
15	7.6	2.8	86
15	1.6	2.7	98
15	2.4	2.0	98
15	4.7	2.0	93
15	2.9	6.7	93
15	2.8	6.7	93
15	5.6	6.3	95
0.5	1.3	5.3	96
0.5	1.4	5.2	96
1	1.4	5.4	94
1	3.0	10.4	95
3	6.5	21.2	92
5	7.3	21.5	90
0	3.3	5.4	85
0	2.0	5.3	89
0	1.9	5.3	87
14	4.4	5.5	88
15	3.1	9.3	89
12	1.7	9.3	93

Average transfer efficiency is 92 per cent.

BIODEGRADABILITY OF ORGANIC COLOUR

Extended carbon bed life requires that the adsorbed organics be easily biodegradable. Pre-ozonation has been cited (19, 31) as a requirement to produce easily biodegradable organics.

Biochemical oxygen demands (BOD_5) were determined on samples of ozonated raw water. The results are presented in Table III:

TABLE III

BIODEGRADABILITY OF OZONATED ORGANICS

Ozone Dose mg/L	Water Colour H.U.	BOD_5 mg/L
0	35	5.6
1	28	7.7
2	22	6.0
4	17	8.0
6	15	10
8	10	10

Dissolved organic carbon (DOC) content of the raw (and ozonated water) was 9.8 mg/L. Considering the ultimate analysis for fulvic and humic acids, oxygen demand should be directly proportional DOC. If the organic colour were rendered completely biodegradable, BOD (total) should be:

$$9.8 \times \frac{32}{12} = 26 \text{ mg/L.}$$

While there is some increase in biodegradability of organic colour, there is no enhancement of activated carbon bed life due to ozone treatment.

MICROBIAL GROWTH

Bacteriological data is summarized as geometric means in Table IV.

TABLE IV

AVERAGE BACTERIA LEVELS

	Raw Water	Ozonated Water	CF Series Effluent	OF Series Effluent	DF Series Effluent
SPC (per mL)	488	63	465	25	80
Total Coliforms	23	4	9	P 50%	24
Background Colonies	1730	13	95	0	20
Fecal Coliform	5	P-100%	P-50%	A	P-20%
Fecal Strep.	12	A	A	A	A

Note: 1) Units are colonies per 100 mL except as noted.

2) P-50% = present in 50 per cent of samples.

3) A = absent.

Ozonation of water with up to 6.5 mg/L ozone did not produce a complete kill of indicator organisms. Bacterial growth was, however, reduced.

The carbon columns exhibited increased microbial growth as indicated by the increase in Standard Plate Count (SPC) from 63 to 465. Bacterial numbers generally increased with increased column age.

Bacteria grow more readily on GAC, comparing SPC's for GAC columns (CF series) vs. sand and anthracite (OF series). If biological colour removal occurs, old GAC should exhibit greater colour removal than old anthracite and sand. Table V presents data for CF-1 (old GAC at 60,000 BV) and OF-1.

TABLE V

BIOLOGICAL COLOUR REMOVAL
COLOUR REMOVED - %

Ozone Dose	CF-1 (GAC)	OF-1 (Anthracite and Sand)
3.9 mg/L	-20	0
2.9	-50	0
2.9	-30	-20
2.9	-10	-10
2.9	-10	-10
3.1	-20	0
3.1	-10	-20
3.1	-40	-20
3.1	-20	-20
4.4	0	0
4.4	0	-20
4.4	20	0
4.4	20	20
4.4	20	20
Averages	-10	0

Raw water temperature was 15°C and ozone residual taken at the filter column influent was less than 0.1 mg/L. Colour removal by the two columns are, statistically, the same. Further, neither the old GAC column nor the old anthracite and sand filter exhibited any significant colour removal.

COLOUR REMOVAL

a) Ozone

Removal of colour by ozone, shown in Table VI, is a function of ozone dose and independent of contact time for the conditions studied. For the range of temperatures encountered, colour removal was also found to be independent of water temperature. Ozone residual did not exceed 0.1 mg/L at any time.

TABLE VI

COLOUR REMOVAL BY OZONE

(Tabulated Values are Per Cent of Influent Colour Removed)

Contact Time - Minutes	Ozone Dose - mg/L					Row Average
	0 to 1.5	1.6 to 2.5	2.6 to 3.5	3.6 to 5.5	Greater Than 5.5	
Less than 4.0	8	38	40	43	64	42
4.0 to 5.9	26	46	58	63	58	43
6.0 to 7.9	31	38	55	62	43	46
8.0 to 10	25	33	52	43	51	41
Greater than 10	22	36	46	47	69	44
Column average	22	38	50	52	57	

The relationship between colour removal and ozone dose is described by the regression equation is:

$$\log_e C_e/C_o = -\ 0.02 - 4.3 \times (\text{mg/L } O_3 \text{ per H.U.})$$

where C_e = effluent colour
C_o = influent colour

b) Activated Carbon

All granular activated carbon (GAC) column runs except CF-2 in Phase 4 were done on pre-ozonated water. Data from CF-2, Phase 4 indicates fractional colour removal from unozonated raw water does not differ from colour removal from ozonated water. Initial colour removal is high (80 per cent or greater) and reducing to about 40 per cent at 300 BV± (bed volumes). This is expected because:

- bed life is determined by total organics adsorbed
- ozonation does not decrease organics content of the water.

Colour removal by GAC is summarized in Table VII. Removal efficiency is strongly influenced by bed age (as total throughput in bed volumes) and slightly by throughput rate (EBCT).

TABLE VII

COLOUR REMOVAL BY ACTIVATED CARBON

(Tabulated Values are Per Cent of Column Influent Colour Removed)

Bed Age - Bed Volumes	Contact Time (EBCT) - Minutes				Row Average
	Less Than 2	2 to 5	5.1 to 15	Greater Than 15	
Less than 200	40	53	77	93	67
200 to 1,000	38	36	46	62	46
1,001 to 5,000	27	27	35	48	34
5,001 to 10,000	23	13	42	31	27
Greater than 10,000	0	-10	0	9	0
Column average	16	24	40	49	

The relationship between colour removal, bed age and throughput rate is described by the regression equation:

$$\mathrm{Log}_e\, C_e/C_o = -0.5 + 0.27\, \mathrm{Log}_e\, X_1 - 0.02\, X_2$$

where C_e = column effluent colour
C_o = column influent colour
X_1 = bed age in 1000 BV
X_2 = EBCT in minutes

At an EBCT of 10 minutes, carbon bed life is calculated at about 10,000 BV.

Using weighted average Freundlich constants of:

$K = 16.6$ mg TOC/g GAC
$1/n = 0.552$

and taking a terminal TOC of 5 mg/L, lg of GAC could adsorb 40 mg of TOC. Alternatively, using the relation developed by Randtke and Snoeyink (37) for humic acid, lg of GAC would adsorb 36 mg TOC. The bulk density of Filtersorb 400 is 420 kg/m^3. Average influent water TOC is taken as 7.5 mg/L. Calculated bed life on adsorption theory is:

$$\frac{420 \times 40}{(7.5-5.0)} \sim \underline{7{,}000 \text{ BV}}$$

c) Dual Media Filtration - OF Series

This series of filter runs was done on ozonated water. Colour removal across these units only was considered.

Colour removal by alum and polymer coagulation of ozonated water followed by direct filtration is presented in Tables VIII and IX.

Colour removal is a function of alum dose, filter rate and water temperature.

TABLE VIII

COLOUR REMOVAL BY COAGULATION/FILTRATION - OF SERIES

(Tabulated Values are Per Cent Colour Removed)

Temperature = 15°C

Filter Rate m/hr	Alum Dose - mg/L Alum/H.U.				Row Average
	Less Than 1.0	1.1 to 1.5	1.6 to 2.0	Greater Than 2	
Less than 6.5	73	80	71	81	76
6.6 to 12	58	75	84	85	76
Greater than 12	22	58	67	79	56
Column Average	51	71	74	82	

TABLE IX

COLOUR REMOVAL BY COAGULATION/FILTRATION - OF SERIES

(Tabulated Values are Per Cent Colour Removed)

Temperature = 0°C

Filter Rate m/hr	Alum Dose - mg/L Alum/H.U.				Row Average
	Less Than 1.0	2.1 to 3.0	3.1 to 4.0	Greater Than 4	
Less than 6.5	77	80	88	82	82
6.6 to 12	62	57	80	80	70
Greater than 12	55	60	72	70	64
Column Average	65	66	80	77	

The relationship between colour removal, alum dose, filter rate and water temperature is represented by the regression equation:

$$\ln X_1 = -2.4 - 1.3 \ln [X_2 \times 1.05^{T-15}] + 0.6 \ln X_3$$

where X_1 = fraction of colour remaining
X_2 = alum dose, mg/L/H.U.
X_3 = filter rate - m/hr
T = temperature - Deg. C.

d) Dual Media Filtration - DF Series

This series of filter runs was done on raw (unozonated) water.

Colour removal by alum and polymer (at 0.5 mg/L) coagulation of raw water followed by direct filtration is presented in Tables X and XI for 15°C and 0°C respectively.

TABLE X

COLOUR REMOVAL BY COAGULATION/FILTRATION - DF SERIES

(Tabulated Values are Per Cent Colour Removed)

Temperature = 15°C

Filter Rate m/hr	Alum Dose - mg/L/H.U.				Raw Averages
	Less Than 1	1.1 to 1.5	1.6 to 2.0	Greater Than 2	
Less than 6.5	35	77	85	88	71
6.6 to 12	57	79	81	85	76
Greater than 12	32	56	78	77	61
Column Averages	41	71	81	83	

TABLE XI

COLOUR REMOVAL BY COAGULATION/FILTRATION - DF SERIES

(Tabulated Values are Per Cent Colour Remaining)

Temperature = 0°C

Filter Rate m/hr	Alum Dose - mg/L/H.U.				Raw Averages
	Less Than 1.5	1.6 to 2	2.1 to 3	Greater Than 3	
Less than 6.5	18	70	80	89	64
6.6 to 12	17	59	69	85	58
Greater than 12	16	42	70	82	52
Column Averages	17	57	73	85	

The relationship between colour removal, alum dosage, filter rate and water temperature is described empirically as:

$$\ln X_1 = -1.4 - 1.6 \ln (X_2 \times 1.05^{T-K}) + 0.02 \ln X_3$$

where X_1 = fraction of colour remaining
X_2 = alum dose in mg/L/H.U.
X_3 = filter rate in m/hr
T = water temperature in Deg. C.

e) Effect of Pre-ozonation on Coagulation/Filtration

Alum dosages based on mg/L alum per Hazen Unit of colour for raw water are less than for pre-ozonated water for equal percentage colour reduction across the coagulation filtration units. For example, an 80 per cent removal across the filters requires:

- 1.3 mg/L alum per H.U. of colour for unozonated water
- 1.6 mg/L alum per H.U. of colour for ozonated water.

However, since pre-ozonated water has only about 20 units of colour, whereas raw water has 35 units alum doses for an overall 80 per cent removal of colour are:

- 45 mg/L alum for raw water
- 26 mg/L alum for pre-ozonated water.

Parallel runs were done in Phases 3 and 4 comparing colour removal from raw and pre-ozonated water at the same operating conditions. The results are summarized in Table XII.

TABLE XII

EFFECT OF PRE-OZONATION

Raw Water Temp. Deg. C.	Alum Dose mg/L	Effluent Colour H.U.
0 (Phase 3)	27	9.5
0 (Phase 3) - ozonated	26	5.2
15 (Phase 4)	34	15
15 (Phase 4) - ozonated	33	3.4

f) Overall Colour Removal

The treatment processes considered in this study are:

- ozone/GAC (CF series);
- ozone/direct filtration (OF series);
- alum coagulation (DF series).

Colour removal by GAC is highly dependent on age of the carbon. Hence, required ozone dose to maintain a 5 H.U. treated water would initially be near zero, increasing after several hundred BV's throughput.

Chemical requirements for colour removal to 5 H.U. colour by ozone/direct filtration are summarized below for a filtration rate of 12 m/hr:

Water Temperature	Ozone Dose	Alum Dose	Polymer
0°C	5 mg/L	40 mg/L	0.5 mg/L
5°C	4 mg/L	39 mg/L	0.5 mg/L
10°C	2 mg/L	44 mg/L	0.5 mg/L
15°C	1 mg/L	44 mg/L	0.5 mg/L
20°C	1 mg/L	34 mg/L	0.5 mg/L

Chemical requirements for colour removal to 5 H.U. effluent colour by alum coagulation/filtration at 12 m/hr are summarized below:

Water Temperature	Alum Dose	Polymer Dose
0°C	123 mg/L	0.5 mg/L
5°C	97 mg/L	0.5 mg/L
10°C	75 mg/L	0.5 mg/L
15°C	59 mg/L	0.5 mg/L
20°C	47 mg/L	0.5 mg/L

IV. COMPARISON OF COLOUR REMOVAL METHODS

GENERAL

Coagulation/filtration of raw water is taken as representative of the conventional colour removal process.

In the following analyses, an average raw water colour of 35 H.U. was used.

CHEMICAL COSTS

a) Unit Costs

The cost of chemicals is based on current (1985) costs at Atikokan. Unit costs of chemicals are:

- Ozone
  - Electrical power cost = 6¢/kWh
  - Power requirement based on a 23 kg/d system operating at 80% capacity
    - Air preparation 100% of 11 kW = 11 kW
    - Ozone generator 80% of 18 kW = 15 kW
    - Off-gas destruction 100% of 1 kW (assume heater on 20% of time) = 1 kW
    - Total energy for 18.4 kg O_3/d = 27 kW

Cost of ozone is

$$\frac{27 \text{ kW} \times 24 \text{ hr} \times 6¢/\text{kWh}}{18.4 \text{ kg} \times 1000 \text{ g/kg}} = \underline{0.211¢/\text{g}}$$

- Alum (liquid) $255/tonne or .0255¢/g
- Polymer 2.0¢/g

- Activated carbon at \$1.45/lb for virgin carbon. (Regeneration is not economically viable.)

Therefore GAC costs $\underline{\$1,400/m^3}$

b) Ozone/Activated Carbon

Average age of the carbon beds was taken as 5,000 BV, with carbon replacement at 10,000 BV. Cost of GAC is therefore:

$$\frac{\$\ 1,400}{10,000} \times 100¢/\$ = 14¢/m^3 \text{ of water treated}$$

At an average bed age of 5,000 BV, colour removal is 50 per cent.

To obtain a 5 H.U. effluent, ozone must produce a colour reduction of 72 per cent. Required ozone dose is 3.9 mg/L (3.9 g/m^3). Cost of ozone is 3.9 x 0.211¢ = 0.82¢/m^3 of water.

Total chemical cost for colour removal is approximately 15¢/m^3.

c) Ozone/Direct Filtration

The total chemical cost of colour removal is:

$$C = 0.211P + 0.0255Q + 1$$

where C = chemical cost in ¢/m^3
P = ozone dose in mg/L
Q = alum dose in mg/L

Polymer cost at 0.5 mg/L is 1¢ per m^3 of water

Costs for combinations of ozone and alum dosages were calculated for temperatures in the range of 0 to 20°C. Minimum costs for each temperature are summarized below.

Filter Rate	Temperature 0°C	 20°C
6 m/hr	2.8¢	1.8/m^3
12 m/hr	3.1¢	2.1¢/m^3
18 m/hr	3.2¢	2.3¢/m^3

d) Conventional Colour Removal

The costs of alum and polymer required to produce an 86 per cent reduction in colour at various filter rates and raw water temperatures summarized below.

Filter Rate	Temperature 0°C	 20°C
6 m/hr	3.9¢	2.1¢/m^3
12 m/hr	4.1¢	2.2¢/m^3
20 m/hr	4.5¢	2.3¢/m^3

e) pH Correction

The raw water is slightly aggressive. Alum coagulation further reduces pH and alkalinity.

Titration curves were prepared for estimating soda ash dosage required for pH correction.

Ozone/GAC (CF series) produces no change in pH or alkalinity. To produce a slightly scale-forming water (Langelier Index = +0.7), requires a soda ash dosage of 15 mg/L. The resultant water has a pH of 9.4.

Ozone/direct filtration (DF series) uses some alum for coagulation of colour. A soda ash dosage of 25 mg/L is required to form a stable water (Langelier Index = +0.7) at a pH of 9.4.

Alum coagulation of organic colour (DF series) requires 35 mg/L soda ash to produce a stable water (Langelier Index = +0.7). Final water pH is 9.4.

Cost of soda ash at Atikokan is $0.94/kg. Costs of pH correction for the treatment alternatives are:

- ozone/GAC, 1.4¢/m^3 of water treated;
- ozone/direct filtration, 2.4¢/m^3;
- alum coagulation, 3.3¢/m^3.

f) Summary of Costs

Chemical costs comparisons for the treatment options studied are presented in Table XIII. Chemical costs for the coagulation/ filtration methods vary with filter rate. Filter rates used in Table XIII are 12 m/hr. Quantity of sludge produced for any option will be proportional to alum dosage. No allowance has been made in chemical costs for sludge disposal.

There is a small decrease in cost for ozone/GAC treatment with increased EBCT.

Chemical costs for colour removal from 35 H.U. to 5 H.U. are summarized in Table XIII. Chemical costs will vary with raw water colour: with high colour during spring run-off, costs will be higher. There are long periods when raw water colour is less than average, resulting in lower chemical costs.

TABLE XIII

CHEMICAL COSTS

Treatment	Water Temp. = 0°C Colour Removal ¢/m^3	 pH Correction ¢/m^3	Water Temp. = 20°C Colour Removal ¢/m^3	 pH Correction ¢/m^3
Ozone/GAC	15	1.4	15	1.4
Ozone/Direct Filt.	3.1	2.4	2.1	2.4
Alum Coagulation	4.1	3.3	2.7	3.3

THM FORMATION POTENTIAL

The raw water has a potential for trihalomethane formation of up to 1 000 ug/L during the testing period.

All treatment processes at chemical dosages which reduced colour to less than 5 H.U. also reduced trihalomethane formation potential to less than 300 ug/L.

V. CONCLUSIONS

All three methods considered; ozone/GAC, ozone/direct filtration and conventional colour removal can produce a water having less than 5 H.U. of colour. Chemical usage in all cases is not economic.

THM formation potential is reduced to acceptable levels (less than 350 ug/L) by all treatment methods when an effluent colour of 5 H.U. is achieved.

There is no apparent microbially mediated removal of colour on GAC or sand.

With no biological regeneration of activated carbon, colour removal is by adsorption only. Cost of chemicals for ozone/ GAC treatment is high, averaging 15¢/m^3 of water treated, made up mostly of GAC replacement costs.

Chemical costs for ozone/direct filtration are lower than for the conventional colour removal process.

There is no clear advantage to ozone treatment prior to alum coagulation for colour removal at Atikokan because of the low cost of alum. However, in addition to the small savings in colour removal chemicals, cost of pH correction is also somewhat lower and sludge disposal costs would be lower.

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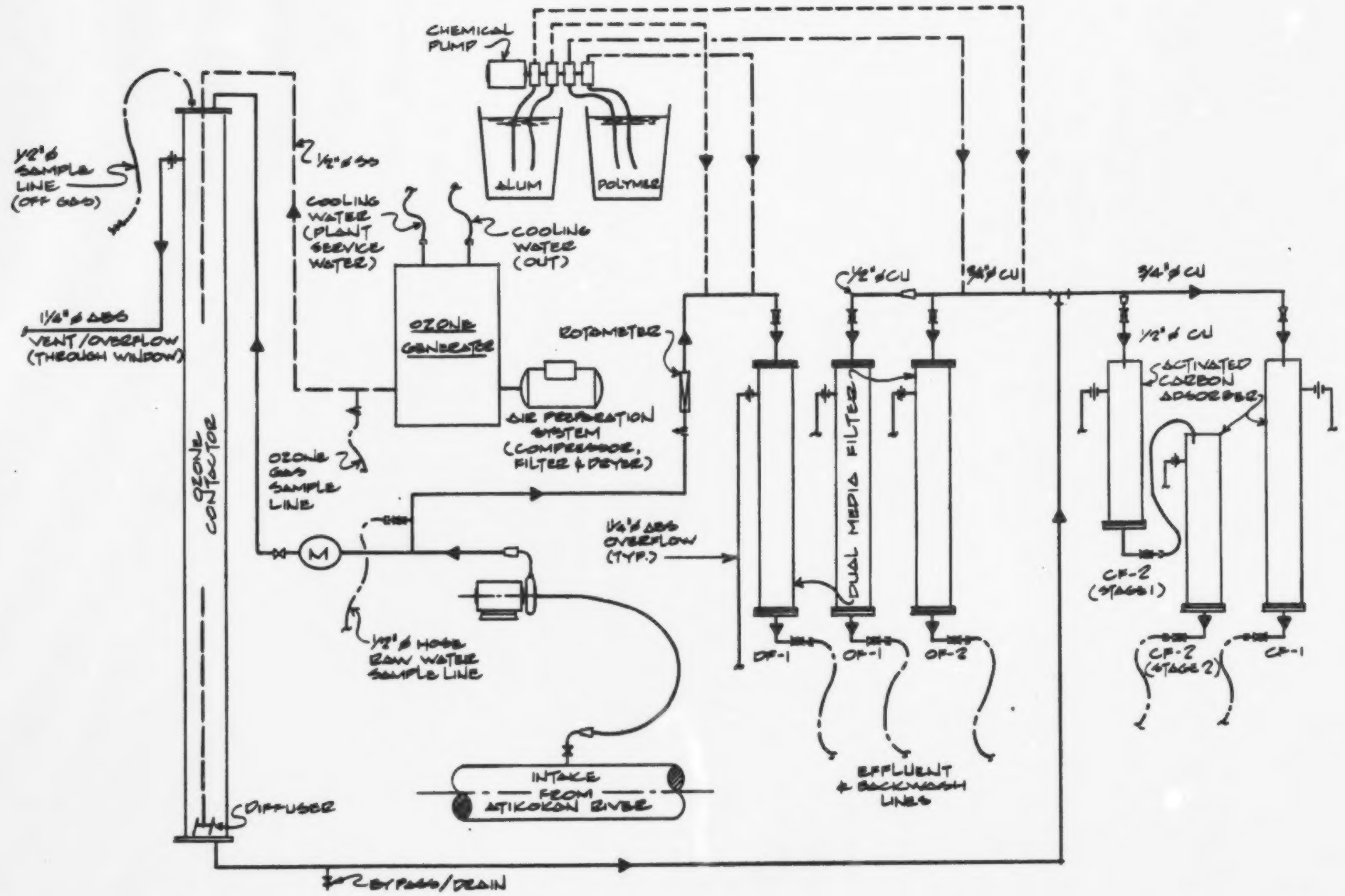

CHEMICAL PUMP
ALUM
POLYMER
1/2"ø SAMPLE LINE (OFF GAS)
1/2"ø SS
COOLING WATER (PLANT SERVICE WATER)
COOLING WATER (OUT)
1 1/4"ø ABS VENT/OVERFLOW (THROUGH WINDOW)
OZONE GENERATOR
ROTOMETER
AIR PREPARATION SYSTEM (COMPRESSOR, FILTER & DRYER)
OZONE CONTACTOR
OZONE GAS SAMPLE LINE
M
1/2"ø HOSE RAW WATER SAMPLE LINE
1 1/4"ø ABS OVERFLOW (TYP.)
INTAKE FROM ATIKOKAN RIVER
DIFFUSER
BYPASS/DRAIN
1/2"ø CU
3/4"ø CU
3/4"ø CU
1/2"ø CU
DUAL MEDIA FILTER
DF-1
DF-1
DF-2
EFFLUENT & BACKWASH LINES
ACTIVATED CARBON ADSORBER
CF-2 (STAGE 1)
CF-2 (STAGE 2)
CF-1

PILOT PLANT (PHASE 1)

DEFLUORIDATION OF AMABELLE TOWNSHIP GROUNDWATER

P.J. Halliday

Proctor & Redfern Limited

Key words: Deflouridation, Groundwater, Amabelle Township.

ABSTRACT

A study of groundwater deflouridation was carried out in August 1985. Two deflouridation processes were selected for evaluation after an intensive literature review. These were:

1. Activated Alumina
2. Reverse Osmosis

Activated Alumina is currently in use in the United States. However, very little data is available on the quality and quantity of regenerant waste produced by the process. Two types of regenerant were evaluated:

1. 1% NaOH Solution

2. Hanfloc (with an equivalent caustic strength to 1% NaOH)

Rapid advances have been made in membrane technology over the past ten years. Reverse Osmosis was evaluated to assess its degree of efficiency and throughput capacity.

The results of both pilot units will be presented, with cost estimates and operational requirements for treating the Amabelle Township ground water.

DEFLUORIDATION

1.0 INTRODUCTION

The presence of fluoride in drinking water may be beneficial or detrimental to public health depending on its concentration (Holden, 1970; Bishop & Sencoucy, 1978). The Ontario Ministry of the Environment (1983) has set a maximum acceptable supply concentration of 2.4 mg/L with a recommended average concentration of 1.2 mg/L which has been shown to reduce dental cavities among children. However, when water supplies contain excessive fluoride concentrations, the teeth of most young consumers become mottled with a permanent black or gray discolouration. Children who drink water containing 5 mg/L or more fluoride are invariably afflicted and, for many, the enamel becomes so severely pitted that they eventually loose their teeth. In fact, bone changes and crippling fluorosis may also result from the long term consumption of water containing fluoride in excess of 8 mg/L (Hodge & Smith, 1954) or from a total intake of 20 mg of fluoride per day for 20 years or more (Roholm, 1937). In Ontario the fluoride concentration in several water supplys can climb as high as 4.0 mg/L.

A number of methods can be used for the removal of excessive fluoride concentrations from water. These can be divided into three categories:

1. Addition of chemicals to cause precipitation or co-precipitation during coagulation

2. ion exchange or adsorption

3. separation by means of a semi-permeable membrane in the removal of Total Dissolved Solids

The chemical methods include the use of lime and alum. Lime can reduce fluoride to no lower than 8 mg/L whereas aluminum sulphate (alum) can reduce fluoride to lower than 1.5 mg/L. However, excessive and costly dosages are required and a sludge disposal problem also occurs.

Adsorption methods include the use of activated carbon, strong base ion exchange resins, bonechar, tricalcium phosphate and activated alumina.

Of these methods, activated alumina appears to be the most commonly used process for fluoride removal due to its relatively high fluoride exchange capacity.

Reverse osmosis utilizing a semi-permeable membrane is primarily used in the reduction of total dissolved solids with fluoride rejections varying from 50 - 95% depending on the membrane utilized.

Based on a literature review carried out prior to the pilot plant study (Appendix A), the activated alumina and reverse osmosis processes were selected for pilot evaluation using a ground water source in the Township of Amabel. This source contains approximately 3 mg/L of fluoride.

2.0 OBJECTIVES

The objectives of the study were to:

- determine the quality and quantity of the regenerant waste stream in the Activated Alumina Process
- determine fluoride rejection of Reverse Osmosis
- determine product water to reject water ratios for Reverse Osmosis
- cost estimates comparing Activated Alumina and Reverse Osmosis for small communities

3.0 METHODOLOGY

3.1 Activated Alumina Process

3.1.1 Chemical Adsorption (Chemisorption)

The difference between physical adsorption and chemisorption is not distinct, although physical adsorption is not specific as to which compounds adsorb and to which sites they are adsorbed. Physical adsorption is associated with weaker bonding energy and is more reversible operating over a longer distance.

Chemisorption, the attraction between adsorbent and adsorbate, is very similar to that of a chemical bond, i.e. higher energy and shorter bond length.

Normally chemisorption cannot accumulate to more than a monolayer due to the specific nature of the bond between adsorbate and surface.

The bond can also be specific to particular sites or functional groups upon the surface of the adsorbent.

In the case of chemisorption of fluoride onto activated alumina, the most important mechanism is electrostatic attraction. This is highly dependent upon pH and ionic strength as can be seen from the optimum pH requirements of fluoride adsorption onto activated alumina of pH 5.5 (Rubel & Woosley, 1979).

Activated Alumina $(Al_2O_3)_n \cdot Al_2O_3$ is calcined granules of hydrated alumina. This material functions as an anion exchanger and the common anions are selected in the following order by acid treated activated alumina (Clifford et. al., 1978)

$OH^- > PO_4^{3-} > F^- > SiO_3^{2-}$;

$Fe(CN)_6^{4-} > CrO_4^{2-} > SO_4^{2-} > Fe(CN)_6^{3-}$;

$Cr_2O_7^{2-} > NO_2^{2-} > Br^- > Cl^- > NO_3^- > MnO_4^{2-} > ClO_4^- > CH_3COO^-$

Activated Alumina reacts in a similar way to weak acid or weak base resins in that both acids and bases must be used for the adsorption -regeneration cycle.

The following equations are a simplistic notation of the complex chemical mechanism involved in the activated alumina process.

When activated alumina is hydrated the following takes place:

$$(Al_2O_3)_n \cdot Al_2O_3 + H_2O \rightarrow (Al_2O_3)_n \cdot (Al_2O_3) \cdot HOH$$

When this neutral hydrated alumina is treated with acid, e.g. sulphuric acid, acidic alumina is formed

$$(Al_2O_3)_n \cdot Al_2O_3 \cdot HOH + H_2SO_4 \rightarrow (Al_2O_3)_n \cdot Al_2O_3 \cdot H_2SO_4 + H_2O$$

When this acidic form is brought into contact with fluoride ions, they displace the sulphate ions.

$$(Al_2O_3)_n \cdot Al_2O_3 \cdot H_2SO_4 + 2NaF \rightarrow (Al_2O_3)_n \cdot Al_2O_3 \cdot H_2F_2 + Na_2SO_4$$

Loading of fluoride is usually best performed under slightly acidic conditions thereby reducing the effects of competing ions such as hydroxyl and silicate and optimizing the fluoride adsorption (Rubel & Woosley, 1978). To regenerate the alumina which is saturated with fluoride, a dilute solution of the most preferred anion, hydroxide, is used (1% sodium hydroxide solution).

$$(Al_2O_3)_n \cdot Al_2O_3 \cdot H_2F_2 + 3NaOH \rightarrow (Al_2O_3)_n \cdot Al_2O_3 \cdot NaOH + 2NaF + 2H_2O$$

The bed is then rinsed to remove excess regenerant and then neutralized with dilute acid.

$$2(Al_2O_3)_n \cdot Al_2O_3 \cdot NaOH + 3H_2SO_4 \rightarrow 2(Al_2O_3)_n \cdot Al_2O_3 \cdot H_2SO_4 + Na_2SO_4 + 2H_2O$$

Acid alumina is then ready for another adsorption cycle.

3.1.2 Treatment Mode for a Clean Bed

The optimum condition for fluoride removal is when the raw water pH is adjusted to between 5.0 and 6.0, with sulphuric acid. Because the amount of acid required is a function of the alkalinity of the raw water, the acid feed rate varies from one water to another.

When raw water pH is adjusted and held at 5.5, the attraction of fluoride to the activated alumina is at its best and interference from competing anions is minimal.

In past studies, as highlighted in the literature review Appendix A, treatment bed capacities have varied from between 4,500 g/m^3 to 9,000 g/m^3. If raw water is above pH 6.0 or below pH 5.0, removal capacity falls dramatically and although efficiency may appear to be the same, breakthrough occurs earlier and treatment runs are shorter. Residence time in the bed is also a limiting factor, with a minimum time of 5 minutes being a practical limit for optimum removal efficiency. Care must also be taken in formation of the bed to prevent wall effect or channelling. Once the pH has been adjusted to 5.5, fluoride level drops rapidly to a very low level and remains this way until breakthrough begins, at which time it increases gradually until the treatment run is terminated. A typical schematic is shown in Figure 1A.

3.1.3 Backwash

Backwash is important for two main reasons before regenerations:

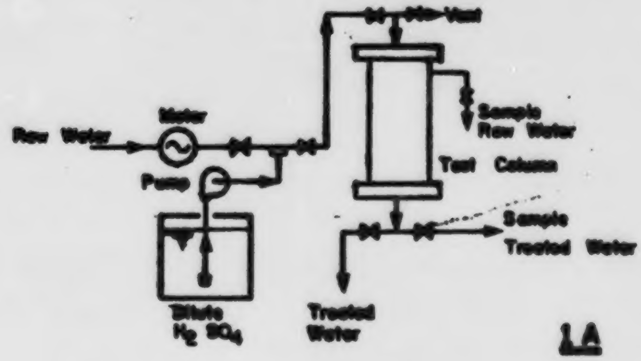
1. any solids which may have been filtered from the raw water by the treatment bed may tend to blind the treatment bed and cause excessive headloss through the filter.

2. Although filtration has not taken place, the fact that there is downward flow through the bed tends to pack the bed. An upflow backwash therefore, expands the bed and prevents any wall effects or channelling to occur. Bed expansion of 50% is adequate, although care must be taken to prevent washout of granular bed material. Ten minutes is generally sufficient for an effective backwash. A typical backwash schematic is shown in Figure 1C.

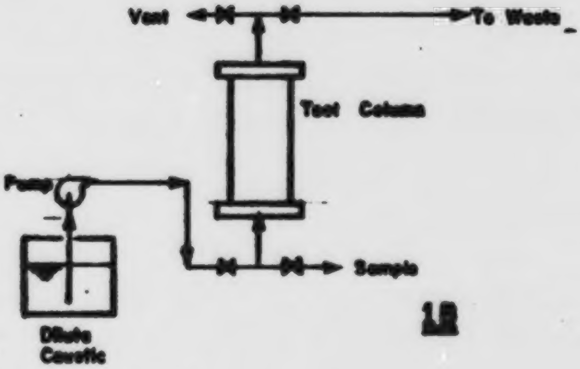
3.1.4 Regeneration

The object of regeneration is to remove all fluoride ions that have been absorbed onto the bed prior to returning the bed to the treatment mode. During the pilot study this was accomplished via an upflow regeneration step utilizing 1% sodium hydroxide solution pumping at a rate of 1 L/min. through a bed volume of 2.27 x $10^{-3}m^3$ for 20 minutes, which is equivalent to 176 litres of 50% sodium hydroxide per cubic metre of treatment media.

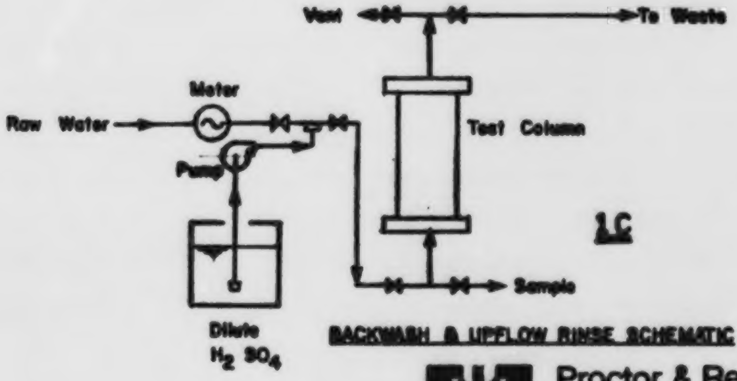
Sodium Aluminate solution (Hanfloc) was tried as an alternative to sodium hydroxide to regenerate the activated alumina, to evaluate if the Hanfloc reduced the activated alumina to the same degree as sodium hydroxide solution. The Hanfloc performed slightly better than the sodium hydroxide in regenerating the bed (Figures 5 and 6). However, insufficient time was available to evaluate its reaction with the activated alumina as compared to the sodium hydroxide, as over a period of 1 year only 5 - 10% of the activated alumina is taken into solution by the 1% sodium hydroxide as sodium aluminate and aluminum hydroxide. A typical regeneration schematic is shown in Figure 1B.


Vent
Raw Water
Meter
Pump
Sample
Raw Water
Test Column
Sample
Treated Water
Dilute
H_2SO_4
Treated
Water
1A

TREATMENT SCHEMATIC


Vent
To Waste
Test Column
Pump
Sample
Dilute
Caustic
1B

UPFLOW REGENERATION


Vent
To Waste
Meter
Raw Water
Test Column
Pump
1C
Sample
Dilute
H_2SO_4

BACKWASH & UPFLOW RINSE SCHEMATIC

Proctor & Redfern Limited
Consulting Engineers and Planners
Toronto

FIGURE Nº 1

3.1.5 Neutralization Mode

The object of this step is to return the bed to acidified activated alumina which in turn neutralizes the bed. During the pilot study, this was carried out by first draining the rinse water to the top of the treatment media and then utilizing an upflow acidification of the bed using 1 N sulphuric acid at a rate of 1 L/min. for 10 minutes. This corrected the bed pH to approximately 8.0. This is equivalent to 120 litres of 1.835 S.G.sulphuric acid per cubic metre of treatment media.

3.1.6 Blending of Treated Water

Blending can take place in a reservoir or in the treated watermain. During a treatment run the fluoride concentration is well below desired levels for long periods of time. As the run nears completion there is a long period of increasing concentration of fluoride in the treated water.

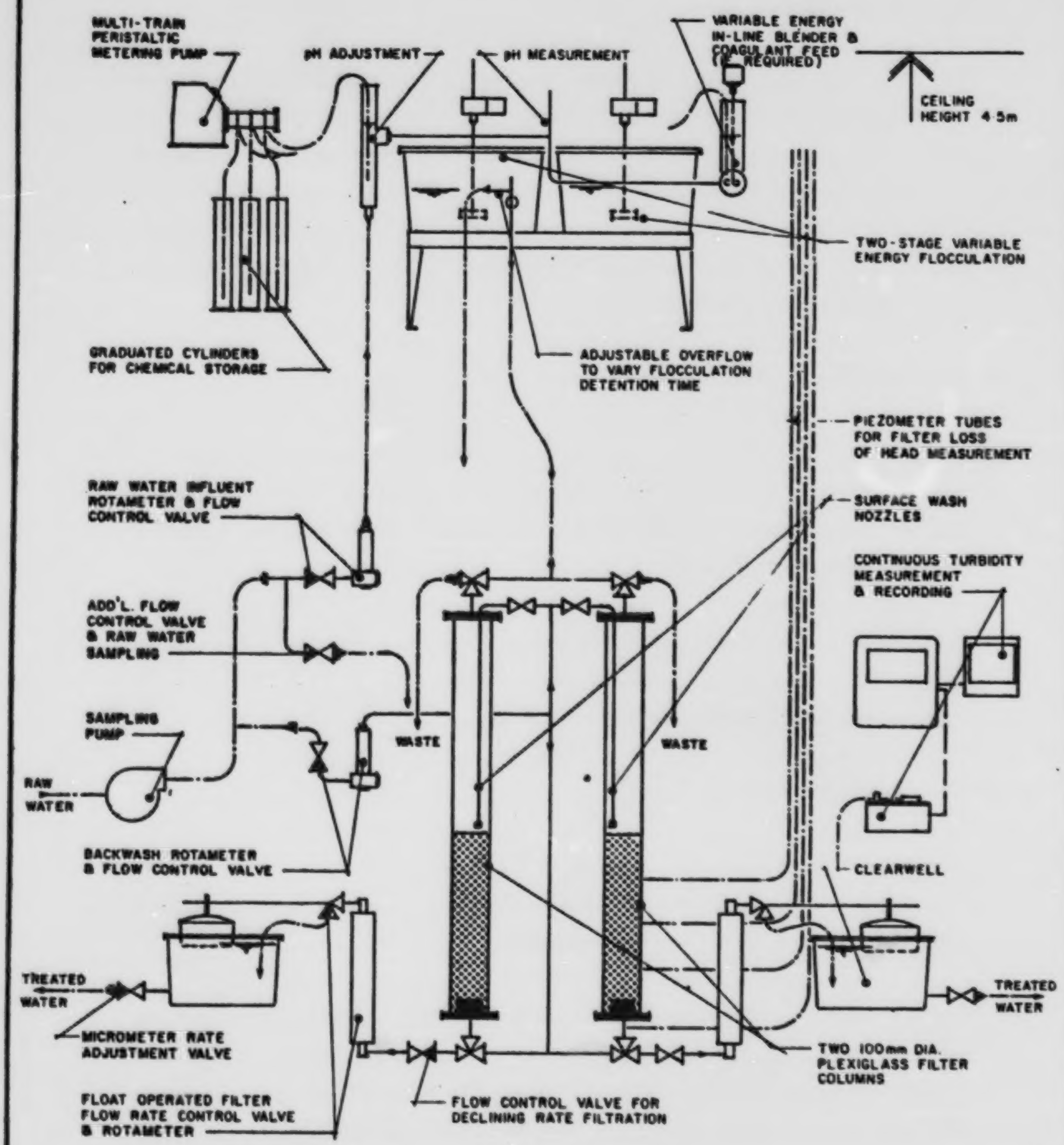
It has been found in past studies (Rubel & Woosley 1978) that a blending of 3:2 or 2:1 gives a combined water quality with an average fluoride concentration meeting the prescribed level.

3.1.7 Activated Alumina Pilot Plant

Raw water for testing was taken from the Birch Street pumphouse prior to the water entering the distribution system for the Daciw and Graham Subdivision (Figure 2) of Amabel Township.

The raw water was then passed through a pH correction chamber where the sulphuric acid required was added, then into a pH measurement chamber. The pH corrected water then flowed by gravity to a 100 mm dia. plexiglass filter column containing a 280 mm deep bed of activated alumina.

The treated water was then discharged to a clear well via a rotameter and float control valve that automatically maintained a constant filtration rate.


MULTI-TRAIN PERISTALTIC METERING PUMP
pH ADJUSTMENT
pH MEASUREMENT
VARIABLE ENERGY IN-LINE BLENDER & COAGULANT FEED (IF REQUIRED)
CEILING HEIGHT 4·5m
TWO-STAGE VARIABLE ENERGY FLOCCULATION
GRADUATED CYLINDERS FOR CHEMICAL STORAGE
ADJUSTABLE OVERFLOW TO VARY FLOCCULATION DETENTION TIME
PIEZOMETER TUBES FOR FILTER LOSS OF HEAD MEASUREMENT
RAW WATER INFLUENT ROTAMETER & FLOW CONTROL VALVE
SURFACE WASH NOZZLES
CONTINUOUS TURBIDITY MEASUREMENT & RECORDING
ADD'L. FLOW CONTROL VALVE & RAW WATER SAMPLING
SAMPLING PUMP
WASTE
WASTE
RAW WATER
BACKWASH ROTAMETER & FLOW CONTROL VALVE
CLEARWELL
TREATED WATER
MICROMETER RATE ADJUSTMENT VALVE
TREATED WATER
TWO 100mm DIA. PLEXIGLASS FILTER COLUMNS
FLOAT OPERATED FILTER FLOW RATE CONTROL VALVE & ROTAMETER
FLOW CONTROL VALVE FOR DECLINING RATE FILTRATION

Pilot Water Treatment Plant

Proctor & Redfern Limited
Consulting Engineers and Planners
Toronto

FIGURE No. 3

A peristaltic pump was used to add the sulphuric acid for pH correction to 5.5. The layout of the pilot plant is shown in Figure 3.

The low bed capacities observed during the trial were a function of less than 5 minutes bed detention time. The small bed utilized during the study was to enable several runs to be evaluated over the week. If a larger bed had been utilized, i.e. enabling 5 minutes detention time, only two runs would have been able to be evaluated during the trial. As previous studies have shown the ranges of bed capacities of activated alumina, it was felt that more runs would enable the objectives of the study to be evaluated more clearly.

Raw water with the pH adjusted to 5.5 was then passed through the bed. The bed begins to remove fluoride at this level and as the bed approaches the optimum pH the water achieves the desired fluoride concentration and becomes usable.

3.2 Reverse Osmosis

Reverse Osmosis is a membrane process which utilizes pressure to drive the feedwater through a semi-permeable membrane whilst a major proportion of the impurity is held back discharged with the waste stream.

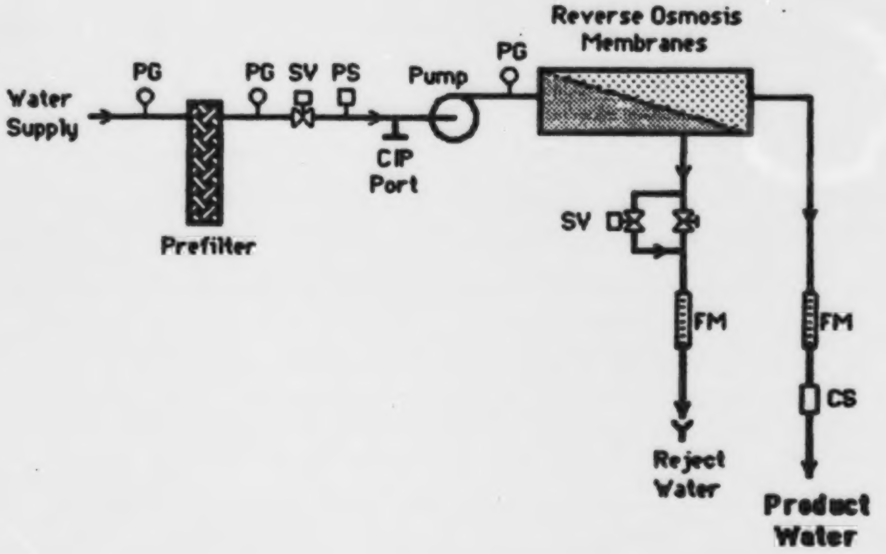
The purified water (known as the permeate) emerges at approximately atmospheric pressure, whilst the waste (known as concentrate) remains at the operating pressure of the system.

During this study, water was pumped at between 675 and 1973 kPa to an NF-40 nanofiltration spiral wound membrane module. This membrane is a T.F.C. (thin film composite) type which possesses performance characteristics between Reverse Osmosis and Ultra-Filtration.

The rejection of impurities varies with the type of impurity and the membrane composition. The degree of performance, i.e. ratio of permeate

ZENO/RO REVERSE OSMOSIS SYSTEMS

WM Series - Flow Schematic


Reverse Osmosis Membranes
PG
PG
PG
SV
PS
Pump
Water Supply
CIP Port
Prefilter
SV
FM
FM
CS
Reject Water
Product Water

NOTES:

1. Number, size and type of membranes varies depending on model.
2. R.O. system operation can be controlled from level switches in a downstream reservoir. Contact supplier for details.
3. Not shown on the schematic are the locations of the check valves, pressure relief valves and aseptic sampling septums.
4. For clean-in-place (CIP), connect gravity feed line from cleaning solution reservoir to CIP port. See operator's manual for complete instructions.

LEGEND:

PG: Pressure gauge; PS: Pressure switch; FM: Flowmeter;
CS: Conductivity sensor; SV: Solenoid valve.

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FIGURE Nº 4

to concentrate volume, varies according to the pressure applied across the membrane.

During the defluoridation study the performance ratio was 30%. If a full scale plant was being designed this ratio could be increased with a resulting loss in efficiency of fluoride removal. However, if fluoride removal is far greater than the desired amount then this approach would be a reasonable method of defluoridation, resulting in a performance ratio of around 70%.

In the first step of the process, water was filtered through a sediment pre-filter to remove the bulk of suspended matter that could interfere with the proper operation of the reverse osmosis membranes.

The heart of the system was a NF-40 nanofiltration spiral wound membrane cartridge. The machine has built-in flushing pressure controls to protect the membrane from abnormal conditions and assure long life.

This particular membrane has a maximum operating pressure of 4100 kPa but a typical operating pressure of approximately 2000 kPa. The membrane that was originally planned for this study was not commercially available. Also a T.F.C. membrane with similar characteristics in terms of rejection as the N.F.-40, is a little "looser" thereby allowing a lower operating pressure, approximately 475 kPa.

A "looser" membrane relates to the pore size and degree of rejection and operating pressure required for the system.

Terminology

Water flux; the quantity of water that can flow through the membrane with units of flow per unit of membrane area per unit of time ($m^3/m^2/d$).

Water recovery; the percent of feed water recovered as product water.

3.2.1 Reverse Osmosis System

The system used was a Zeno/RO Reverse Osmosis System, Model WM240 that incorporates prefiltration and reverse osmosis (RO) as the key process functions and includes an advanced design solid state control system (Figure 4).

The equipment has the following specifications:

Output

The system produces 240 litres/hour of treated water with a 25°C feedwater. Product water recovery is variable between 25% and 45% depending on feedwater composition, temperature and operating pressure.

Prefiltration:

The system includes a 10" polypropylene filter (5 micron nominal rating) in a polypropylene housing.

Reverse Osmosis Pump:

The system includes a bronze rotary vane pump with a 3/4 hp ODP motor to boost feed pressure up to the 1360 kPa operating pressure.

Reverse Osmosis Membrane Assembly:

The system includes one (1) only 4" diameter x 40" long spiral wound thin-film composite membrane.

Control System:

The system includes a single control panel with solid state circuitry in a Nema 1 enclosure. The operating mode (Off, Run, Wash, Flush) is selected via toggle switches for Power (on/off); RO pump (run/standby/reset); Wash cycle (on/off) and Flush Cycle (auto/off/manual). In Auto flush mode, a 2 minute low pressure/high velocity flush of the membrane is initiated every 2 hours.

Instrumentation:

The system includes a dual range digital conductivity meter for the product water with internal temperature compensation to 5°C and an adjustable maximum acceptable conductivity setpoint. Other instrumentation includes 3 oil-filled pressure gauges indicating prefilter inlet/outlet and RO membrane pressures and 2 flowmeters indicating product/reject flowrates.

Valves:

Flow Regulating Valve: The system includes a stainless steel adjustable needle valve located on the reject line to allow setting of the correct operating pressure and recovery.

Feedwater Solenoid Valve: The system includes a feedwater solenoid valve that automatically opens whenever water is required.

Frame/Shroud:

The system is supplied on a sturdy frame designed for wall mounting (optional floor stand is available). A shroud encloses the front and sides of the system. Both the frame and the shroud are of steel construction with an enamel painted finish.

Feedwater Requirements:

The feedwater must have a silt density index less than 5, a pH within the range 2 - 11, a temperature less than 40°C, a free chlorine residual less than 0.1 mg/L and a pressure (when system is in operation) of greater than 204 kPa.

Physical Specifications:

Materials of Construction: All components are made of inert non-corroding material.

External Connections: For plumbing connections, the system includes a 1/2" NPT fitting for feedwater, and 1/2" OD compression fittings for product, reject and clean in place inlet. The electrical service required is 110 Volt, 15 or 30 amp, single phase, 60 Hz, 0.8 kW.

4.0 DESCRIPTION OF TEST SITE

4.1 Physical Description of Amabel

Amabel is the southernmost township in the Bruce Peninsula. It is bounded by the townships of Albemarle to the north, Keppel to the east, and Arran to the south. On the west lies Lake Huron. The Township is roughly rectangular in shape, about 11 kilometres from east to west, and about 28 kilometres from north to south. It contains about 28,486 hectares.

The most important single factor affecting the climate of Amabel is the location of the Township adjacent to the waters of Lake Huron, producing a modification of climatic conditions. Its latitude, approximately 44 degrees north, places the Township in the path of the prevailing Westerly winds as well as on the route followed by the majority of cyclonic storms, producing an effect of marked changeability in weather conditions. Amabel has a mean annual temperature of 6 degrees Celsius with the maximum occurring in July and averaging 19 degrees Celsius. The minimum occurs in February with an average temperature of -8 degrees Celsius.

There are several inland lakes in Amabel. The largest are Boat, Chesley, Gould, Isaac and Spry Lakes.

Glacial action some 55,000 years ago is responsible for the landforms of the Township. The area from Concession 7 down to Highway 21 is a drumlinized till plain. As the last glacier (the Wisconsin Glacier) inched its way over the area it pushed huge mounds of rock before it. Some of this debris would slip under the "snout" of the glacier and be plastered on the bedrock in a thick layer composed of a mixture of material from the largest boulder to the finest clay. This layer is "till"; in some cases, well-borings indicate it to reach a depth of over 100 feet. On these till plains are the elongated hills known as "drumlins". In shape they are like the inverted bowl of a spoon; they are often called "whalebacks". Drumlins are formed on till plains where there is an abundance of clay. It is believed that as the glacier advanced, it overrode some impediment, and that the materials being carried on the lower part of the glacier became plastered against the impediment, slowly building up to an oval-shaped mound. The long axis of each of these hills points to the direction from which the glacier advanced. Between the drumlins the land is low and poorly-drained; Chesley and Gould Lakes are contained in two of these low areas. The Sauble River winds its way around the drumlins. These low, rounded hills give the southern part of the Township its beautiful, rolling landscape.

Besides the till plain, the two other main land areas in Amabel are a sand plain and a limestone plain.

The sand was deposited by a glacial lake, Lake Algonquin, which once covered the Township north of the drumlinized till plain. When the Lake receded, the sand was exposed; it covers much of the central part of the Township. One well-known feature of the Sauble Beach area is the sand dunes, which extend north. The dunes are built up of sand carried from the mouths of the Saugeen and Sauble Rivers. Behind the dunes is a series of small, shallow lakes - among them Boat, Spry and Patterson - ponded there as a result of the absence of drainage through the dunes to Lake Huron.

The 'Limestone plain was created when advancing glaciers plastered a thin veneer of till material over the bedrock. Most of this till is less than five feet deep. Soils developed on this material often suffer from poor drainage and excessive stoniness. There are numerous bogs.

In the Township of Amabel there are several water aquifers with differing water qualities ranging from high sulphide and coloured water to excellent water quality with only the fluoride concentration being in excess of the MOE guidelines.

The water supply selected for the study was the well that feeds the Daciw and Graham Subdivisions at Sauble Beach in the Township of Amabel.

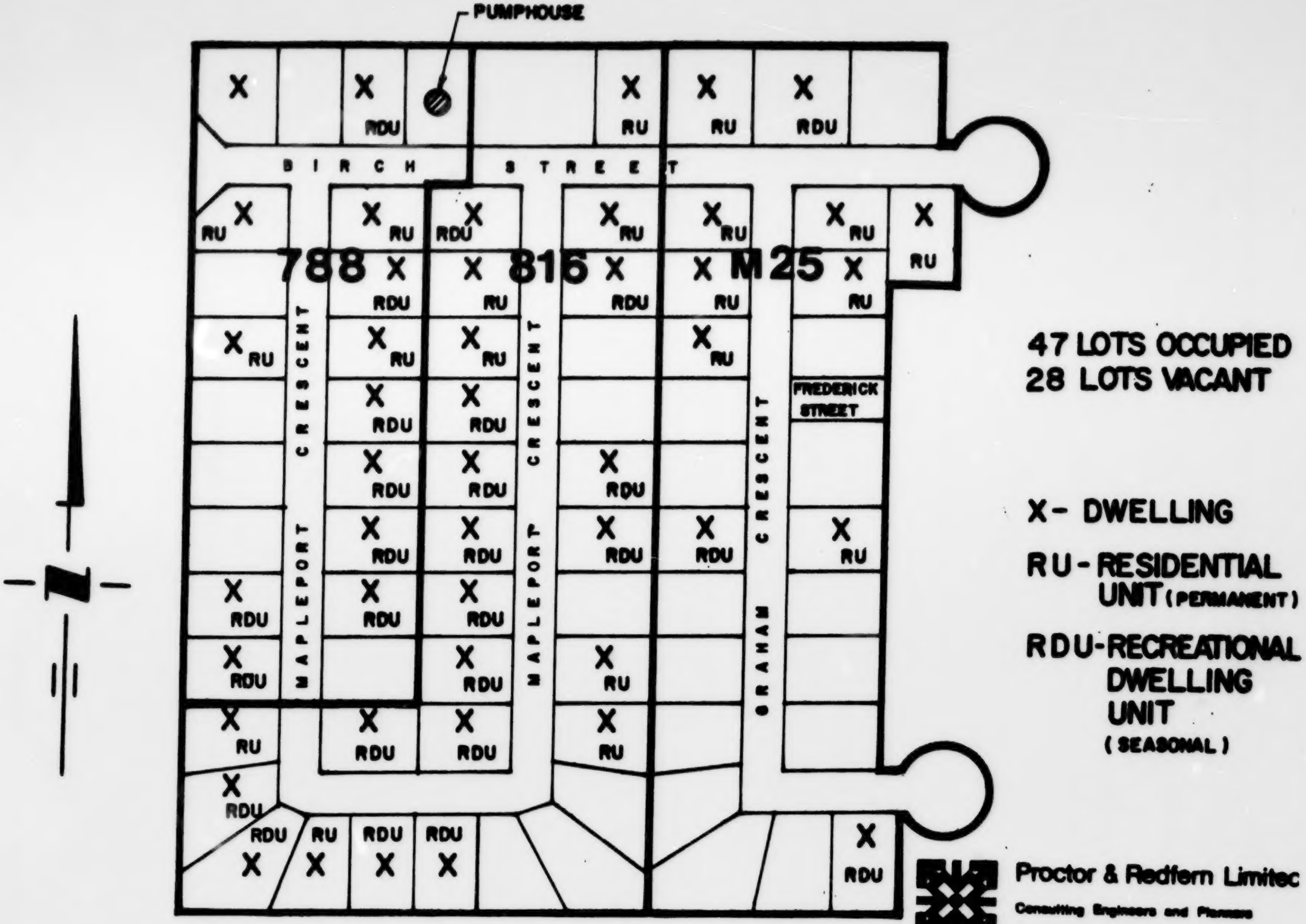
PUMPHOUSE
BIRCH STREET
MAPLEPORT CRESCENT
MAPLEPORT CRESCENT
GRAHAM CRESCENT
FREDERICK STREET
788
816
M25
X
RU
RDU
47 LOTS OCCUPIED
28 LOTS VACANT
X - DWELLING
RU - RESIDENTIAL UNIT (PERMANENT)
RDU - RECREATIONAL DWELLING UNIT (SEASONAL)
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FIGURE Nº 2

5.0 EXPERIMENTAL RESULTS

Data for the pilot study is tabulated in Tables 1, 2 and 3 Appendix B. The pilot study consisted of five adsorption cycles in the activated alumina bed as well as continuous reverse osmosis to enable comparison of the two different processes.

5.1 Activated Alumina

Run No. 1 had a flow rate of 3 L/min through an alumina bed volume of 7.3 x 10^{-3} m^3 (0.085 cu.ft.), equivalent to a filtration rate of 25 m/hr (8.3 IGPM/sq.ft) and resulting in a sigma factor of 0.001 mg/mg.

The sigma factor is denoted as follows:

$$\text{Sigma } (\sigma) = \frac{\text{Mass Fluoride removed} \quad (\text{mg})}{\text{Mass of Activated Alumina} \; (\text{mg})}$$

Run No. 2, utilizing a flow rate of 1.5 L/min or a filtration rate of 12 m/hr (4 IGPM/sq.ft.) resulted in a sigma factor of 0.0008. This run resulted in the lowest sigma factor and was due to the fact that the bed was not acidified to show that the acidification step is required to activate the alumina prior to a treatment run.

Run No. 3 utilized a flow rate of 2 L/min or a filtration rate of 18 m/hr (6 IGPM/sq.ft.) resulting in a sigma factor of 0.01.

Run No. 4 utilized a flow rate of 1 L/min or a filtration rate of 9 m/hr (3 IGPM/sq.ft.) resulting in a sigma factor of 0.001.

Run No. 5 utilized the same conditions as Run No. 3 with only the regenerant stream being changed to sodium aluminate solution resulting in a sigma factor of 0.001.

The following bed capacities were noted:

Run 1 = 1500 g/m^3
Run 2 = 1200 g/m^3
Run 3 = 2000 g/m^3
Run 4 = 1500 g/m^3
Run 5 = 2150 g/m^3

Analysis of the regenerant waste streams are noted in Table 3 with fluoride concentrations ranging from 85 - 250 mg/L.

5.2 Reverse Osmosis

The pilot study utilizing the R.O. unit was basically operated at two pressures:

1. 675 kPa
2. 1975 kPa

At 675 kPa the water flux was 0.2 m^3/m^2/d with a water recovery of 12% and a fluoride removal rate of 80%.

At 1975 kPa the water flux was 0.8 m^3/m^2/d with a water recovery of 32% and a fluoride removal rate of 80%.

With the membrane utilized in this study the recovery was 30% which is a low recovery rate. However, in a full scale application the recovery rate could be raised to in excess of 70% by using a looser membrane which was not commercially available for the trial, which is more closely related to the membrane types used for ultrafiltration.

6.0 COST ESTIMATES

Operating and Capital cost estimates are based on the pilot study results. Cost estimates have been developed using the following data.

1. Treatment flow rate - 455 L/d/person.
2. Average fluoride conc of raw water - 3 mg/L.
3. Average fluoride conc of treated water - 0.3 mg/L.
4. Minimum fluoride capacity of activated alumina - 2000 g/m^3.
5. Activated alumina - $2.34/kg
6. 50% caustic soda - 24¢/L.
7. 1.835 S.G. sulphuric acid - 23¢/L.
8. Amount of 1% caustic required per regeneration - 10 bed volumes.
9. Amount of 1 N sulphuric acid required per neutralization - 5 bed volumes.
10. Cycle duration - 3 days.
11. Backwash based on 50% bed expansion.

It is also assumed that the treated water is blended with raw water at the ratio of 3:2 to obtain an average fluoride concentration of 1.4 mg/L.

6.1 Operating Labour Costs

6.1.1 Activated Alumina Plant

This area is the most difficult to quantify. The operator is required to be dependable and competent with a degree of experience in chemical handling. However, the operator is not required full time for the system except for the days when regeneration takes place.

Therefore the plant will require approximately 20 hours/week.

6.1.2 Reverse Osmosis Plant

The operator is required to be dependable and competent, but does not require the same degree of experience in chemical handling as an operator for the activated alumina system. Operator attention at the plant is basically 1 hour a day except when the plant has to be flushed and cleaned.

Therefore the plant will require aproximately 10 hours/week.

Utility costs for both systems are minimal however the activated alumina plant will consume more power due to the greater number of pumps, etc. involved with the process.

Activated Alumina = $\$0.01/m^3$
Reverse Osmosis = $\$0.005/m^3$

6.2 Activated Alumina

Capital Costs for Small Activated Alumina Defluoridation Systems

Item	Population 1000	Population 5000
Treatment vessels	$30,000	$ 70,000
Treatment media	2,500	11,700
Pipe fittings etc. & instrumentation	4,000	7,000
Chemical storage tanks	5,000	8,000
Chemical pumps	5,000	8,000
Installation of equipment	30,000	50,000
Building	40,000	80,000
Engineering & Contingencies	17,500	35,200
Total	$134,000	$269,900

Physical Size of Treatment Vessels & Storage Tanks

Item	Population 1000	 5000
Activated Alumina Filters	3 x 0.9 m dia x 2.5 depth	7 x 1.8 m dia x 2.5 m depth
50% Caustic Soda Tank	2 x 5.0 m^3	3 x 10.0 m^3
1.835 S.G. Sulphuric Acid	2 x 5.0 m^3	3 x 10.0 m^3

Filters are sized to give a media bed of 0.9 m x 1.0 m for 1,000 population and 1.8 m x 1.0 m for the 5,000 population to maximize media bed efficiency.

Operating Conditions for a Small Activated Alumina Defluoridation Plant

Item	Population 1000	 5000
Plant Flow	455 $m/^3/d$	2273 m^3/d
Raw Water Fluoride Conc	3 mg/L	3 mg/L
Treated Water Fluoride Conc	0.3 mg/L	0.3 mg/L
Sigma Factor (O)	0.005	0.005
Activated Alumina	1000 kg	5000 kg
Min. Capacity of Activated Alumina	2000 g/m^3	2000 g/m^3
Cycle Duration	3 days	3 days
Volume of 1% sodium hydroxide/cycle/filter	4000 L	8200 L
Volume of 1N sulphuric acid/cycle/filter	2000 L	4100 L
No. of Filters	3	7
No. of Filters in Operation	2	5
Labour	$240/week	$240/week
Utility	$0.01/$m^3$	$0.01/$m^3$

Chemical Costs

Sodium Hydroxide	$ 7,000/annum	$ 35,000/annum
Sulphuric Acid	$ 4,500/annum	$ 22,500/annum
Activated Alumina	$ 2,340/annum	$ 11,700/annum

Labour	$12,480/annum	$ 12,480/annum
Utility	$ 1,660/annum	$ 8,296/annum
Operating Costs	16¢/m^3	11¢/m^3

6.3 Reverse Osmosis Cost Estimate

Reverse Osmosis System for Population of 1,000

- 32 of 8 in. dia. x 40 in. long membranes
- 8 of F.R.P. pressure vessels
- 1 of 60 H.P. stainless steel centrifuge pump
- 1 of 5 micron prefilter system

Dimensions: 20" L x 36" W x 60" H

Price - $278,000

Total Membrane replacement cost (over 5 year term)

$114,000

Reverse Osmosis System for Population of 5,000

Four (4) units each consisting of:

- 40 of 8 in. dia. x 40 in. long membranes
- 10 of F.R.P. pressure vessels
- 1 of 45 H.P. stainless steel centrifugal pump
- 1 of 5 micron prefilter system

Dimensions: 200" L x 36" W x 60" H

Unit Cost = $292,000

Total Cost = $1,168,000

Total membrane replacement cost $456,000 (over a 5 year term)

Operating Costs

	1000 Population	5000 Population
Membrane replacement	20,800	83,200
Utility	830	4,150
Labour	6,240	6,240
Total	**27,040**	**89,440**
Operating cost	16¢/m^3	11¢/m^3

7.0 CONCLUSIONS

The results of the study were as follows:

1. Determine quality and quantity of regenerant waste stream in the activated alumina process.

   The quality of the waste stream is documented in Table 3, showing fluoride concentrations ranging from 85 - 250 mg/L depending on the length of run time and fluoride removal achieved. The quantity of waste stream was equivalent to 9.0 m^3 of 1% sodium hydroxide per cubic metre of activated alumina.

   The higher fluoride levels observed in the regenerant wastes of runs 4 and 5 would seem to indicate that the Hanfloc solution is more efficient in regenerating the bed. However, further pilot studies would have to be carried out to evaluate this point more closely.

2. Determine fluoride removal of reverse osmosis.

   During the trial a fluoride removal of 80% was achieved.

3. Determine product water to reject water ratios for reverse osmosis.

   At 675 kPa the water recovery ratio was 12%.

   At 1975 kPa the water recovery was 32%.

   These recovery ratios are low and can hopefully be improved upon by a "looser" semi-permeable membrane which will become commercially available in the near future.

4. Cost Estimates comparing Activated Alumina and Reverse Osmosis for Small Communities

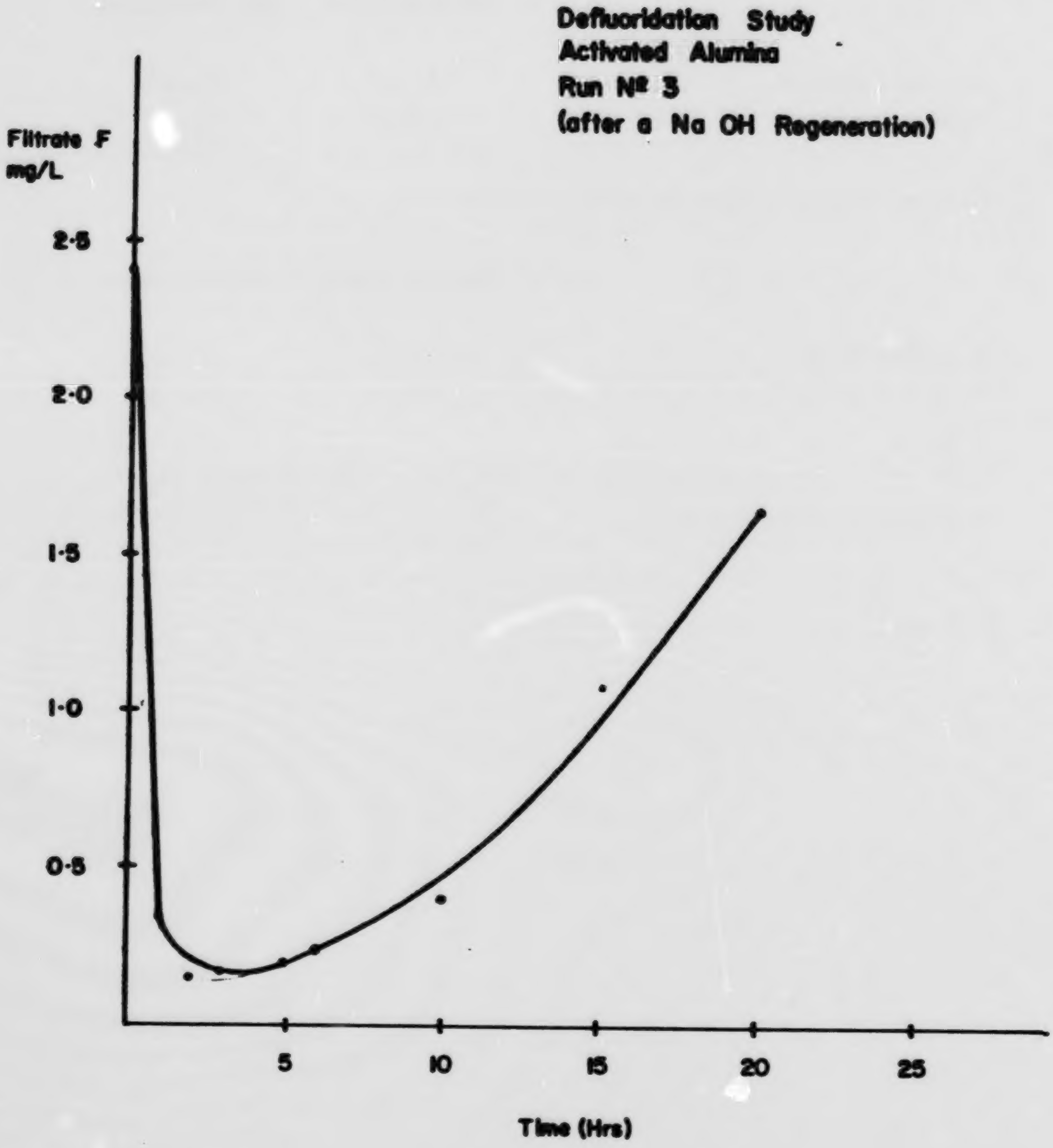
From the cost estimates carried out it would appear that both plants have the same operating costs.

	1000 Population	5000 Population
Activated Alumina	16¢/m^3	11¢/m^3
Reverse Osmosis	16¢/m^3	11¢/m^3

However the capital costs are significantly different.

	1000 Population	5000 Population
Activated Alumina	134,000	269,900
Reverse Osmosis	278,000	1,168,000

Therefore from a purely economic viewpoint, the activated alumina system appears to be the most viable.



Defluoridation Study
Activated Alumina
Run Nº 3
(after a Na OH Regeneration)

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FIGURE Nº 5

Defluoridation Study
Activated Alumina
Run Nº 5
(after a Hanfloc Regeneration)

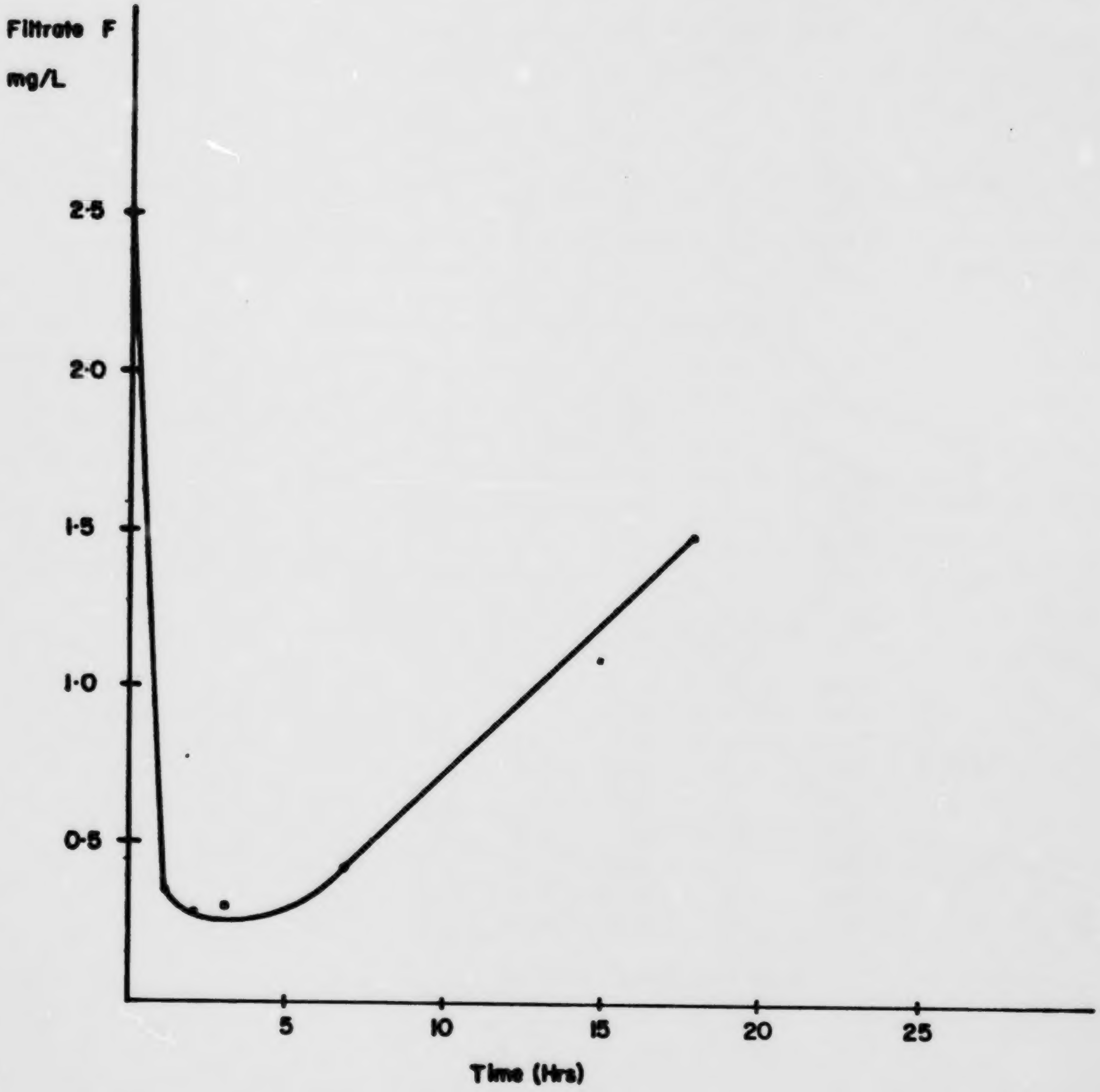

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FIGURE Nº 6

TABLE 1

ACTIVATED ALUMINA PILOT PLANT ANALYSIS

			pH		Fluoride		Removal	
Date	Time	Filt Rate L/m	Raw	Filt	Raw	Filt	mg/L	mg
Aug 5	13:30	3	8.1	6	2.65	0.35	2.3	414
	14:30	3	8.2	5.4	2.6	0.19	2.41	434
	15:30	3	8	5	2.5	0.34	2.16	389
RUN 1	16:30	3	8.1	4.9	2.57	0.6	1.97	355
	17:30	3	8.2	5.1	2.6	0.85	1.74	315
	18:30	3	8.1	5	2.5	1.05	1.45	261
Aug 6	9:30	3	8.2	5.3	2.45	2.1		
Total F removed = 2168 mg sigma = 0.001								
	12:00	1.5	8.1	7.3	2.49	0.85	1.64	148
	13:00	1.5	8	4.9	2.5	0.48	2.02	182
	14:00	1.5	8.1	5.3	2.45	0.4	2.05	185
	15:00	1.5	8	5	2.65	0.41	2.24	202
RUN 2	16:00	1.5	8	5.3	2.48	0.39	2.09	188
	17:00	1.5	8	5.4	2.6	0.45	2.15	194
	18:00	1.5	8.1	5.5	2.75	0.52	2.25	203
	22:00	1.5	8.2	5.1	2.45	1.35	1.15	414
Aug 7	9:00	1.5	8	5.4	2.55	2.3		
Total F removed = 1716 mg sigma = 0.0008								
	15:00	2	8.3	6.3	2.6	0.35	2.25	270
	16:00	2	8.1	5.4	2.55	0.15	2.4	288
	17:00	2	8	5.2	2.47	0.18	2.29	275
RUN 3	18:00	2	8.1	5.5	2.5	0.2	2.3	276
	19:00	2	8.2	5.3	2.55	0.25	2.3	276
	20:00	2	8.1	5.4	2.5	0.28	2.22	266
	23:00	2	8	5.1	2.45	0.42	2.03	244
Aug 8	9:00	2	8.1	5.3	2.5	1.65	0.85	1020
	10:00	2	8.1	5.4	2.65	1.85		
	11:00	2	8.2	5.3	2.6	2.05		
Total F removed = 2915 mg sigma = 0.001								

	15:00	1	8	7.3	2.6	0.4	2.2	132
	16:00	1	8.1	5.4	2.55	0.18	2.37	142
	17:00	1	8.2	5.3	2.5	0.15	2.35	141
RUN 4	18:00	1	8.2	5	2.45	0.18	2.27	136
	19:00	1	8.1	5.4	2.55	0.2	2.35	141
	22:00	1	8.1	5.3	2.65	0.32	2.33	419
Aug 9	9:00	1	8	5.4	2.45	1.05	1.4	924
	10:00	1	8.1	5.3	2.5	1.2	1.3	78
	11:00	1	8	5.2	2.5	1.35	1.2	72
	12:00	1	8.1	5.4	2.55	1.55		
	13:00	1	8.2	5.4	2.5	1.7		

Total F removed = 2185 mg sigma = 0.001

	16:00	2	8.1	6.8	2.45	0.65	1.8	216
	17:00	2	8	5.5	2.4	0.35	1.05	126
RUN 5	18:00	2	8.1	5.4	2.55	0.28	2.27	272
	19:00	2	8	5.3	2.5	0.3	2.2	264
	23:00	2	8	5.4	2.5	0.42	2.08	250
Aug 10	10:00	2	8.1	5.3	2.5	1.2	1.3	1716
	11:00	2	8.2	5.4	2.45	1.35	1.1	132
	12:00	2	8.1	5.4	2.4	1.55	0.85	102
	13:00	2	8	5.3	2.5	1.8		

Total F removed = 3078 mg sigma = 0.001

TABLE 2

REVERSE OSMOSIS PILOT PLANT ANALYSIS

Date	Prefilter Press kPa	R.O. Press kPa	Flow L/min			F mg/L		Conductivity Mhos
			Concentrate	Permeate	Raw	Conc.	Perm.	
3/8/85	340	680	11.5	1.5	2.6	3.0	0.5	58
4/8/85	340	680	11.5	1.5	2.6	2.85	0.5	62
5/8/85	612	1972	9	4	2.5	3.6	0.6	70
6/8/85	578	1972	9	4	2.5	3.3	0.5	66
7/8/85	612	1972	9	4	2.5	3.2	0.5	68
8/8/85	544	1972	9	4	2.5	3.3	0.5	69
9/8/85	599	1972	9	4	2.4	3.2	0.5	66

TABLE 3

QUALITY OF WASTE REGENERANT STREAM

Sample	Run	pH	Alkalinity	Hardness	F-	Al^{3+}	SO_4^{2-}
Raw	1	8.1	159	78	2.6	N.D.	
Regenerant Waste	1	10.2	-	-	85	145	3900
Raw	2	8.1	133	80	2.6	N.D.	-
Regenerant Waste	2	9.9	-	-	91.5	114	5200
Raw	3	8.1	129	88	2.6	N.D.	
Regenerant Waste	3	11.9	-	-	120		
Raw	4	8.1	133	80	2.45	N.D.	
Regenerant Waste (Hanfloc)	4	12.5	-	-	202		
Raw	5	8.1	135	82	2.5	N.D.	
Regenerant Waste (Hanfloc)	5	12.7	-	-	250		

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SEDIMENT AND POLLUTANT ACCUMULATION IN THE HUMBER RIVER MARSH, TORONTO, ONTARIO

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Key words: Humber River, Sediment, Contaminant Accumulation.

ABSTRACT

As part of the Toronto Area Watershed Management Strategy or TAWMS study, sediment and contaminant accumulation in the Humber River Marsh was evaluated. The study area consists of a low energy fluvial system bounded by Lake Ontario in the south and Bloor Street in the north. Sediment cores were collected from the channel, floodplain and backwater pond environments present in the Marsh during the fall of 1983, and laboratory analyses were performed during the fall of 1984 and spring of 1985.

Recent sedimentation rates as measured by stratigraphy, pollen and lead-210 radioisotope analysis ranged from as low as 0.2 cm/yr. on the floodplain to as high as 1.9 cm/yr. in the backwater ponds. Cores were subsampled and tested for specific trace metals, polychlorinated biphenyls (PCBs), and the pesticide DDT and its metabolites DDD and DDE. Metal concentrations ranged from below detection limit to 7, 108, 79, 970, 85, and 190 ug/g for Cd, Cu, Cr, Mn, Ni, and Pb, respectively. Organic pollutant concentrations ranged from below detection limit to 163.4, 65.0, 93.9 and 21.3 ng/g, respectively for PCBs , DDT, DDD and DDE.

With the exception of Pb in all cores and Cd in one core, metal contamination was not considered to be significant (i.e., surface metal concentrations were not significantly greater than assumed background levels). With respect to PCBs, DDT, DDD and DDE sediment contamination was considered to be moderate. It is estimated that approximately 3000 kg of lead, 3.2 kg of PCBs, 0.4 kg of DDT, 1.3 kg of DDD and 0.4 kg of DDE are presently stored in the Humber Marsh. In general, sediments from the backwater ponds had the highest contaminant concentrations, reflecting finer sediment texture and possible point sources of pollutants. The study indicates that contaminated sediments have been accumulating on the floodplain and in the backwater ponds for some time and, given present conditions, are likely to continue to do so. In general, the channel area does not represent a significant storage area for contaminated sediments. Further research into Humber River sediment quality is needed to monitor future changes in sediment quality and to pinpoint pollutant sources.

Abstract

Historical sedimentation rates, the concentration and spatial distribution of six trace metals (Cd, Cr, Cu, Mn, Ni and Pb), PCB's DDT, DDD and DDE, and the mass of Pb, PCB's, DDT, DDD and DDE were determined for the Humber Marsh, Toronto. Eight sediment cores were collected in the fall of 1984 and spring of 1985 (two from the channel, two from the levees and four from the backwater ponds). Sedimentation rates measured by stratigraphy, pollen, or radio isotopes ranged from 0.2 - 0.3 cm/yr on the levees and from 0.9 - 1.9 cm/yr in the backwater ponds. Seven cores were subsampled and tested for trace metals, PCB's and pesticide. Cadmium concentrations ranged from below detection limit to 7 ug/g, nickel from 17 - 85 ug/g, copper from 10 - 79 ug/g, chromium from 30 - 108 ug/g, lead from 12 - 190 ug/g and manganese from 420 - 970 ug/g. Organic pollutant concentrations ranged from below detection limit (1 ng/g) to 21, 65, and 94 ng/g for DDE, DDT and DDD, respectively, and from below detection limit (10 ng/g) to 163 ng/g for PCB's. Concentrations of contaminants were generally higher in backwater pond sediments than in floodplain or channel sediments. The exception was DDT which was present at highest concentrations in the channel sediments. The results indicate that both metal and organic pollutants have been accumulating in the sediments of the Humber Marsh for at least 30 years. Contaminated sediments presently stored in the Marsh are a potential source of pollution for Humber Bay if they become remobilized. The presence of pollutants in surface sediments is a reflection of poor water quality in the Humber River which flows into Lake Ontario near several public beaches. The Humber Marsh is also a popular recreational area and valuable wildlife habitat; the presence of pollutants in the sediments may be incompatible with these uses.

Acknowledgements

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1. Introduction

Since 1981 the Humber River has been the focus of several studies dealing with water quality as part of the Toronto Area Watershed Management Strategy Study (TAWMS). One of the tasks of the study is to evaluate sediment and contaminant movement in the Humber River. The present study deals with pollutant accumulation and sedimentation rates in the lowermost reach of the Humber River, south of Bloor Street (known as the Humber Marsh). The study was initated in September 1984 and fieldwork was carried out between October of the same year and February of 1985.

The objectives of the study were three-fold:

1) to determine historical sedimentation rates in the Humber Marsh

2) to establish the concentration and spatial distribution of pollutants in the sediments

3) to calculate the total mass of pollutants stored in the Marsh.

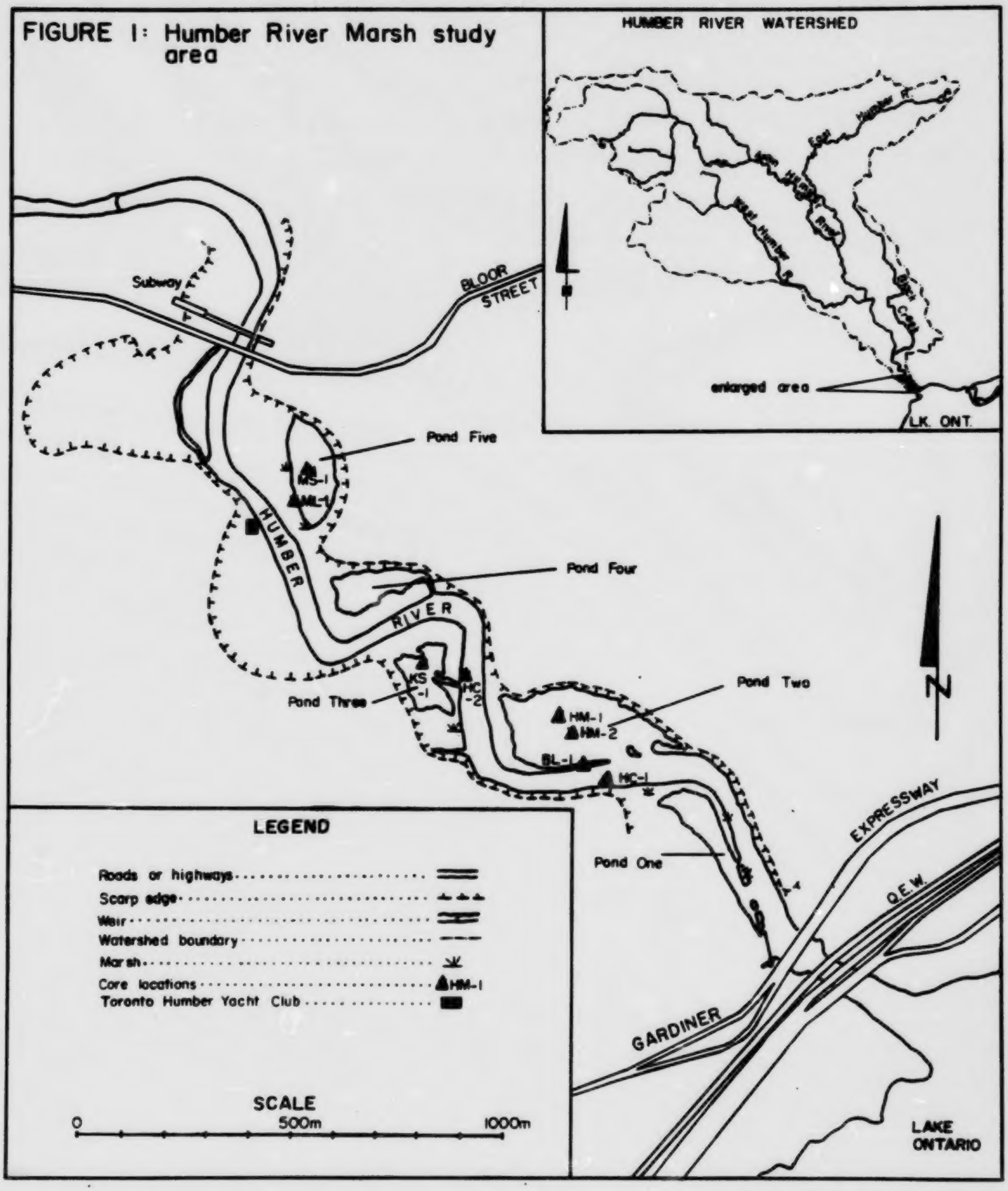
2. Description of Study Reach

The Humber River drains an area of 897 square kilometers, rising in the morainic hills east of Orangeville and flowing in a southeasterly direction towards Lake Ontario. The upper part of the watershed is mainly rural in character whereas the lower portion (south of Steeles Avenue) is urbanized. Industrial land use is mainly concentrated along the reach bordered by Steeles Ave in the north and Black Creek in the south. Potential sources of metal and organic pollution in the Humber watershed include industrial discharge, combined sewar outflow, agricultural runoff, as well as, urban and rural storm runoff. A more detailed description of the watershed is provided elsewhere.[1]

The study area consists of the lowermost reach of the Humber River and adjacent floodplain, from Bloor Street downstream to Lake Ontario, refered to in this report as the Humber River Marsh. (Fig. 1). During moderate summer flows, channel width and depth average 55.0 m and 1.48 m, respectively. The average slope of the bed in the study reach is 0.05 %, substantially less than the average slope of the reach immediately upstream (0.40 %).[2] The morphology of the study reach is that of a drowned river valley in which the longitudinal river profile has continuously adjusted to rising base level by depositing sediment. The wedge of sediment which now underlys the Marsh varies in depth from 1.2 m near Bloor Street.[2] to over 20 m at Lake Ontario[3]. Pollen, radiocarbon and stratigraphic evidence from the Humber Marsh indicate that this valley-fill has been accumulating over the past millenia, in response to rising base levels in the Lake Ontario basin.[4] On a more recent time scale, examination of archival maps (the earliest dated 1834 AD) confirms that the plan form of the river in the study reach has changed little in the past 150 years. Thus, the Humber Marsh appears to have existed in its present form for some time.

In the past century aggradation in the Humber Marsh area has accelerated in response to the higher sediment yields associated with

FIGURE 1: Humber River Marsh study area


HUMBER RIVER WATERSHED
East Humber R.
Main Humber R.
West Humber R.
Black Creek
enlarged area
LK. ONT.
Subway
BLOOR STREET
Pond Five
MS-1
ML-1
HUMBER RIVER
Pond Four
Pond Three
KS-1
HC-2
Pond Two
HM-1
HM-2
BL-1
HC-1
Pond One
EXPRESSWAY
Q.E.W.
GARDINER
LAKE ONTARIO
N
LEGEND
Roads or highways
Scarp edge
Weir
Watershed boundary
Marsh
Core locations HM-1
Toronto Humber Yacht Club
SCALE
0
500m
1000m

urbanization and land use change. The magnitude of this process can be assessed both directly and indirectly. Sediment stratigraphy and pollen and isotope accumulation rates provide direct quantitative information. Indirect information is provided by personal communications with local residents and members of the Toronto Humber Yacht Club (THYC), and from air photographs (the earliest taken in 1937). Most sources reveal that sediment is actively accumulating on the floodplain in response to annual overbank flow events.

3. Sedimentary Environments

Three major sedimentary environments can be identified in the Humber Marsh study area they are: the channel, the backwater ponds and the levee-floodplain (Fig. 2).

3.1 Channel

In the study reach the Humber River meanders between steep valley walls. Flow divergence at the begining of the reach, where bed slope decreases, results in lower velocities and a reduced capacity to transport sediment. Here the channel is wider and deeper than farther upstream in order to accommodate the slower moving water as it nears Lake Ontario.

The results of the 1984 TAWMS study entitled "Physical Characteristics of the Humber River" indicate that loosely consolidated clay and silt deposits, ranging in depth from 0.10 - 0.20 m near Bloor St. and from 1.5 - 2.0 m near the Queen Elizabeth Way, overly sand and more highly consolidated clay and silt in the Humber channel. This indicates that sediment is stored, at least temporarily, in the channel within the study reach. Due to continued isostatic readjustment the level of Lake Ontario is rising at a rate of approximately 20 cm per century, or 0.2 cm/yr.[5]. Thus a similar long term deposition rate can be expected in the Humber River channel. In the short term however, seasonal fluctuations in lake level (on the order of 50 cm) exert a major control on sediment deposition and erosion in the channel. It can also be expected that sediment and associated pollutants from the channel will be flushed lakeward during high flows and during spring breakup when ice scours the bottom of the channel. It is also important to note that since construction of the Clairville dam on the west branch of the Humber River in 1964 and construction of the lower Humber weirs in 1966, peak flows and ice block formation have been reduced and the residence time of sediments in the channel has

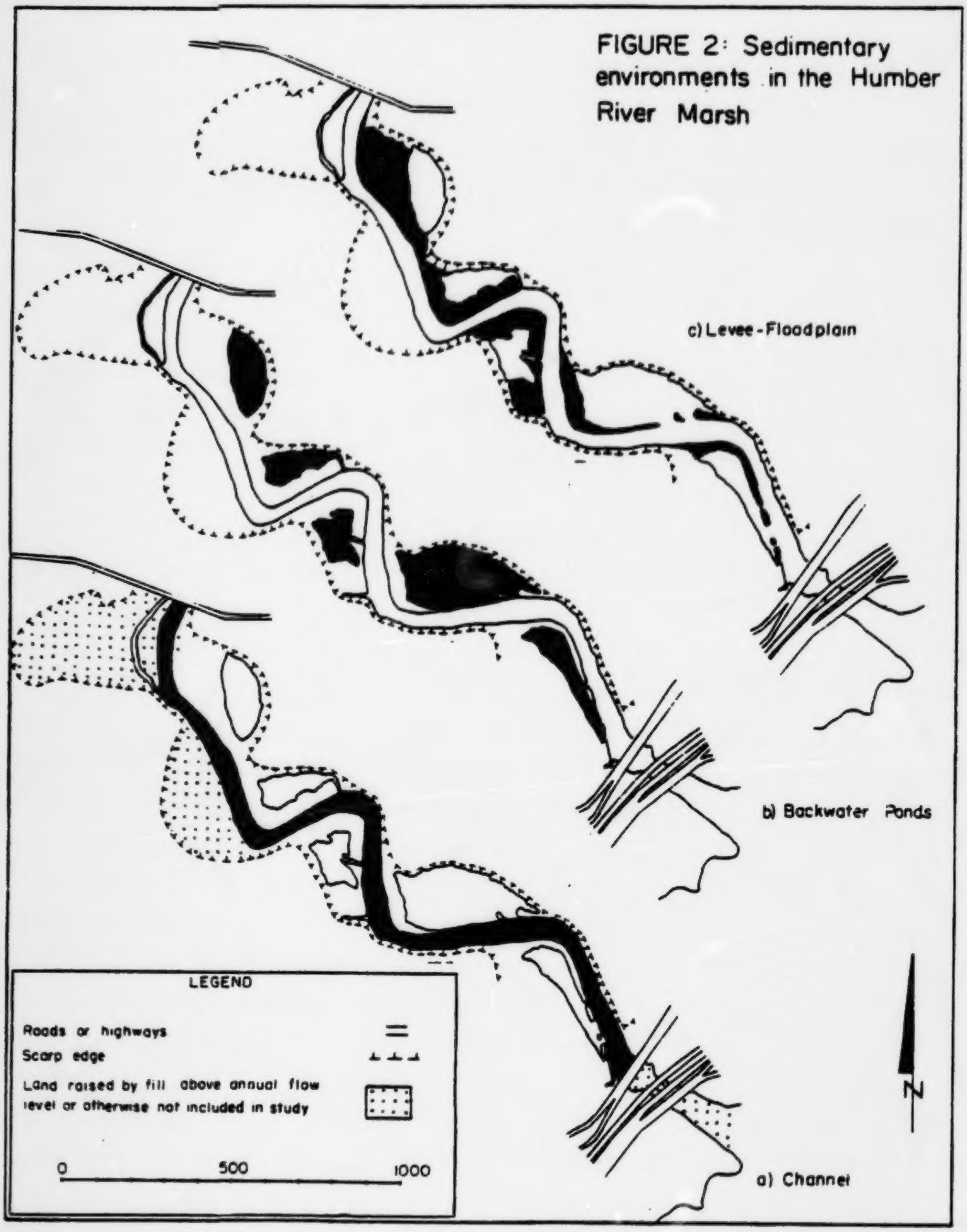


FIGURE 2: Sedimentary environments in the Humber River Marsh

c) Levee-Floodplain
b) Backwater Ponds
a) Channel
LEGEND
Roads or highways
Scarp edge
Land raised by fill above annual flow level or otherwise not included in study
0
500
1000
N

probably increased.

3.2 Backwater Ponds

Figures 1 and 2 show five depressions bordering the Humber River within the Marsh. In this report these depressions are referred to as 'backwater ponds'. These ponds receive water and sediment directly from the channel during times of high flow. Ponds Two and Three dryed out during the summer of 1984 while the others contained water too deep to freeze to the bottom during the following winter. Sediment delivery to these backwater ponds is seasonal; however, because they commonly contain standing water, very fine sediment is able to accumulate. Although some erosion may occur during unusually large flows events, the backwater ponds have experienced the most continuous deposition of any area within the Marsh. They are also the most likely sites for the accumulation of pollen and the pollutants associated with fine-grained sediments.

3.3 Levee-Floodplain

In addition to the channel and backwater areas two other sedimentary environments exist. Levees and floodplain-like surfaces are gradually being built up through the processes of overbank flooding and the deposition of fine-grained material. The levees bordering the channel are subject to the most frequent inundation and help to cut off the backwater ponds. The remainder of the land that is also being built up by overbank flooding and deposition is identified here as floodplain. Both the levees and the floodplain receive sediment and associated pollutants only intermittently, for much of the year they are subaerial surfaces covered with cattails (Typha spp.) and other types of vegetation. Hence these areas are less likely to accumulate pollen and pollutants than the backwater ponds.

4. Methods

4.1 Sample Collection and Preservation

Representative coring sites for the determination of contaminant accumualtion were selected from the three sedimentary environments in the Marsh. Two cores (HC-1 and HC-2) were taken from the channel area, two (BL-1 and ML-1) from the levee-floodplain, and four (KS-1, MS-1, HM-1 and HM-2) from the backwater ponds. The approximate coring locations are shown in Fig. 1. No cores were taken from the floodplain-like areas on the west side of the river adjacent to and directly upstream from the Toronto Humber Yacht Club (THYC) . The area upstream is well above mean annual flood level and is not actively accumulating sediment. The area adjacent to the THYC has been raised by the dumping of substantial amounts of fill. Neither of these areas is considered to be representative of the Marsh environment. The channel island between Bloor St. and the THYC was also excluded from the study.

Seven sediment cores were collected during October and November of 1984 using a 4.7 cm diameter, modified Livingstone-type sampler. These cores were either subsampled immediately upon return to the laboratory or were stored in a cool place overnight (4° C) and subsampled the following day. After extruding a core it was described lithologically, then eight or nine 2 cm wide intervals were removed at mechanical, and lithologically appropriate, intervals. Each 2 cm high disk was then divided into three parts. One half of each disk was placed in a sterile, amber glass jar, sealed with an aluminium foil lined cap and stored (< 5 days) at 4° C until shipment to a laboratory for pesticide and PCB analysis. The remaining portion of the disk was split in half again and each quarter stored in a preweighed, sterile glass jar at 4° C. Within three days these samples were oven dried at 100° C to determine moisture content. One of the quarters was used for metal analysis while the remaining quarter was stored in plastic for approximately three months before being submitted for radiochemical analysis.

An additional core was taken from Pond Two during Febuary of 1985 using a 4.7 cm diameter Livingstone-type sampler. This core was extruded in the field and later described and subsampled for pollen and radiochemical analysis in the laboratory.

Table 1 provides a summary of coring site information and analyses.

4.2 Analytical Procedure

Diagnostic Research Laboratories analysed the samples for specific trace metals. They tested for Cr, Cu, Mn, Ni, and Pb by direct current plasma emission spectroscopy and for Cd by atomic absorption spectroscopy. All samples were digested in hydrochloric, nitric and perchloric acids before metal analysis was performed. National Bureau of Standards River Sediment No. 1645 was used as a control.

Mann Testing Laboratories analysed the samples for the presence of PCB's, 4,4-DDT, 4,4-DDD and 4,4-DDE using dual capillary gas chromatography equipped with two electron capture detectors. Positive identification of DDT, DDD and DDE was based on chromatograms and partial mass spectra. Quantification of PCB mixtures was determined by summing the peak heights of the mass spectra of 10 individual PCB congenors and comparing these to the sum of the corresponding peaks in an appropriate, recently analysed Arochlor standard*.

Flett Research Laboratory (Winnipeg, Manitoba) performed the radio chemical analysis. Briefly, Pb-210 is a naturally occurring radioactive isotope of the Uranium-238 decay series. Decay of the isotope ^{226}Ra yields the inert gas ^{226} Rn which eventually disintegrates into ^{210}Pb. In the analysis of aquatic sediments, the

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*The PCB's detected in the samples resembled the Arochlor 1254 standard

Table 1: Summary of Coring Site Information and Analyses Performed.

Core	Location	Sampling Date	Sedimentary Environment	Water Depth (cm)	Core Length (cm)	Pb-210	Analyses Metal and Organics	Pollen
MS-1	Pond Five	841025	backwater pond	40	91	yes	yes	no
KS-1	Pond Three	841025	backwater pond	—[*]	78	yes	yes	no
HM-1	Pond Two	841115	backwater pond	55	72	yes	yes	no
ML-1	edge of Pond Five	841025	floodplain	N/A	73	yes	yes	no
BL-1	west of Pond Two	841101	levee	N/A	84	yes	yes	no
HC-1	west of Pond Two	841115	channel	45	40	no	yes	no
HC-2	east of Pond Three	841115	channel edge	N/A	63	no	yes	no
HM-2	Pond Two	850209	backwater pond	53	> 200	yes	no	yes

[*] Marsh Three was seasonally dry when core was taken.
N/A = not applicable

^{210}Pb produced by the decay of naturally occurring ^{226}Rn is termed the 'supported ^{210}Pb'. Excess or 'unsupported ^{210}Pb' is added to the sediment column primarily via the atmosphere as a bi-product of anthropogenic activities including the burning of coal and the use of leaded gasoline. Once incorporated into the sediment ^{210}Pb decays in accordance with its half life of 22.26 years. Sedimentation rates can be determined from the decay of the unsupported component. The amount of unsupported ^{210}Pb is determined from the difference between the total ^{210}Pb activity and the supported ^{210}Pb, the latter of which is determined by assay of the daughter Po-210 which is assumed to be in secular equilibrium with the parent. In the analysis Po-210 was added as a standard to determine process efficiency.

Analysis for pollen and total carbon was carried out in the Botany Laboratory of the Royal Ontario Museum by the writer under the supervision of Dr J.H. McAndrews (curator). Sediment moisture content was determined by oven drying at 100 °C. Organic carbon and $CaCO_3$ content were determined from weight loss at 550 °C and 1000 °C respectively. Between 1 and 2 mls of sediment from each level was spiked with a known number of Lycopodium spores and then processed by the standard treatment with HCl, KOH, HF and acetolysis. The resulting concentrate was stained with safranin and mounted in silicone oil. If sand was present the sample was sieved through 15 and 150 um screens before mounting in silicone oil. Pollen concentration was estimated from the ratio of fossil pollen to added Lycopodium . Pollen and spores were identified by comparison with a modern pollen reference collection and with the aid of an illustrated key[6].

Lithologic description was based on hand texturing and visual assesment. Due to the number of analyses performed on each sample interval and the mass of sediment required for the analyses. Mechanical grain size analysis would have been desireable but, due to limitations in the study, could not be carried out.

5. Results

5.1 Stratigraphy and Sediment Accumulation Rates

5.1.1 Core Stratigraphy

The stratigraphies of eight cores lifted from the Humber Marsh are shown in Fig 3. The lithology of each core was determined by hand texturing and visual assessment before samples were removed for pollutant or pollen analysis. The lengths of cores obtained for pollutant analysis ranged from 41 cm (HC-1) to 91 cm (MS-1). An additional core obtained for pollen analysis was 11 m long; however, only the upper 2.3 m are shown here. On the basis of lithology the cores can be divided into two groups. Sediments from cores HC-1 and HC-2, lifted from the channel area, are predominantly sand and silt with some pebbles, organic matter and shells (gastropods). Frequent variations in grain size, associated with fluctuating discharge, occur. The remaining cores were obtained from still water or subaerial environments. Silt and clay predominate, although peaty sediments do occur (ie. at the bottom of BL-1), and grainsize variations are gradual and infrequent.

In all cores not obtained from the channel area an anomalous sand layer occurs less than 60 cm below the surface . This sand is associated with high energy flow conditions and it is probable that it was deposited during the last major flood on record, that caused by Hurricane Hazel in October 1954. If this assumption is made then the year 1954 can be assigned to the sand unit and the overlying deposits would represent deposition since that time. The top of the sand unit was arbitrarily chosen as the upper limit of deposition, even though it is probable that finer sediments were deposited on top of the sand during the same event, because it was a well defined boundary . Thus the 30-year net sedimentation rates calculated for the cores (see Table 2) are maximum possible rates (rates are not corrected for compaction which may have occurred during sampling).

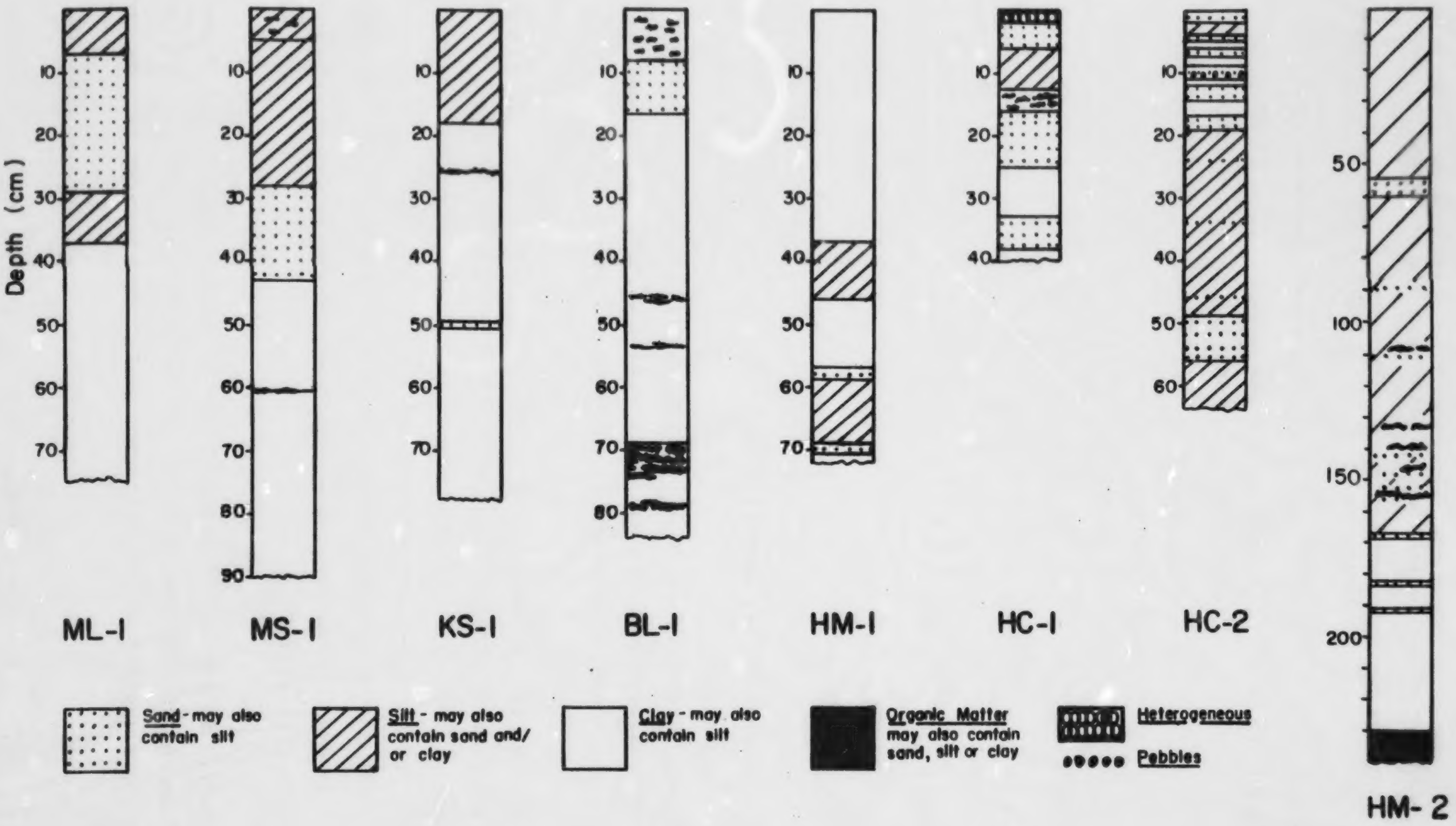

Fig. 3: Stratigraphy of sediment cores from Humber Marsh (note change of scale on far right

Table 2: Thirty Year Sedimentation Rates for Humber Marsh Sediment Cores

Environment	Core	Thickness of sand layer (cm)	Depth to sand layer (cm)	30-year sedimentation rates (30 cm/yr)
Backwater Ponds	HM-1	2	57	1.9
	HM-2	4	56	1.9
	KS-1	1	50	1.7
	MS-1	15	28	0.9
Levee	ML-1	22	7	0.2
	BL-1	9	8	0.3

Subaqueous (backwater pond) sedimentation rates are greater than subaerial (levee-floodplain) ones (Table 2). Within similar environments, however, sedimentation rates are generally comparable.

The two cores lifted from Pond Two (HM-1 and HM-2) are stratigraphically similar (ie. both are predominantly clayey-silt and both have a sand layer between 50-60 cm). This suggests that the sediment facies observed in these two cores are locally continuous. This finding supports the assumption the stratigraphy of indiviual cores is more or less representative of the stratigraphy of the areas from which they were taken.

In summary, sedimentation rates in the backwater ponds ranged between 1 - 2 cm/yr over the past 30 years while sedimentation rates on the adjacent levees and floodplain were less than 1 cm/yr for the same period.

5.1.2 Pollen Analysis

The distribution of Ambrosia (ragweed) pollen in aquatic sediments from eastern North America provides a marker for estimating modern sediment accumulation rates. Ragweed is a weedy herb which commonly invades disturbed ground. A marked increase in the occurrence of Ambrosia pollen in recent sediments is generally associated with historical deforestation and human settlement. In southern Ontario the ragweed rise has been dated at 1850[7] AD. and its occurrence allows for an estimation of average sediment accumulation rates over the past 135 years.

Figure 4a shows the occurrence of ragweed pollen as a percentage of total tree pollen in the upper 2.3 m of sediment from core HM-2. Pollen density and thermal analysis are also shown. On the basis of the sudden increase in Ambrosia percentages, historical sedimentation can be inferred to have begun at approximately 190 cm below the surface. One hundred and ninety centimeters of deposition in 135 years yields a net sedimentation rate of 1.4 cm/yr. The latter value is less than the 30-year sedimentation rate for the same core (see Table 2). If sedimentation occurred at the higher rate of 1.9 cm/yr during the last 30 years then, in order to obtain a net sedimentation rate of 1.4 cm/yr over the entire 190 cm, the average sedimention rate between 1850 and 1954 (60-190 cm) would have to have been less than 1.4 cm/yr.

Additional evidence supporting the claim that sediment above 190 cm was deposited since 1850 is provided by the pollen density calculations and thermal analysis (Figs. 4b and 4c). Pollen density decreases dramatically between 180 and 200 cm. This trend is largely a function of increased sediment yields in the watershed, which is related to land clearance , rather than any substantial decrease in the delivery of pollen to the sediments. Above 190 cm, percent residue is greater than below 190 cm also indicating increased delivery of clastic material to the Marsh.

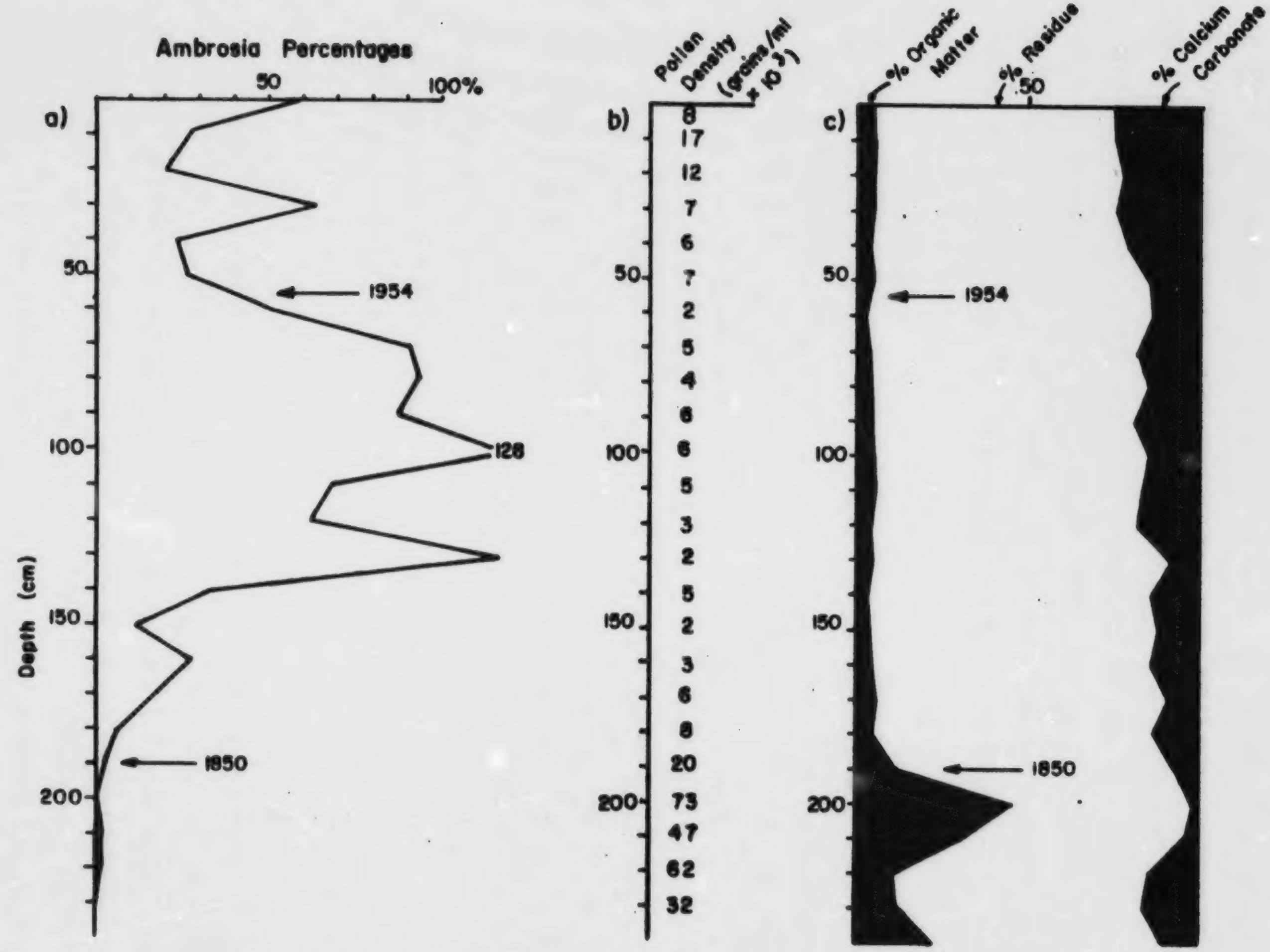

Fig. 4: Ambrosia pollen percentages (a) calculated on the basis of total tree pollen, pollen density (b), and thermal analysis results (c) from core HM-2.

Additional pollen analysis performed on a core taken from Pond Five indicates that the Ambrosia rise occurs between 80-90 cm below the surface. The resulting 135-year sedimentation rate of 0.6 cm/yr is slightly less than the 30-year sedimentation rate (0.9) calculated for the same Pond (see MS-1, Table 2). The difference in depth to the Ambrosia rise between Ponds Two and Five is a reflection of the proximity of Pond Two to the channel and to Lake Ontario.

On a much longer time scale, a radiocarbon date of 3800+/- 80 years BP from 1030 - 1040 cm below the surface of the Marsh yields a long-term average sedimentation rate of 0.2 cm/yr for sediment below 190 cm. Comparison of long-term and historical sedimentation rates in Pond Two suggests that there has been a seven-fold increase in the average rate of sedimentation in the past 135 years. This increase can largely be attributed to historical land use practices in the Humber watershed since 1850. Initially, land clearance and agricultural practices caused increased sediment yields, later urban development was the main contributor. The rapid development of large areas of the Humber River drainage basin, such as Etobicoke and Brampton/Bramalea, in the 1970's could explain why the 30-year sedimentation rates are higher than the average sedimentation rate for the entire period since 1850.

5.1.3 Lead-210 dating

Lead-210 isotope analysis is one method of dating sediments deposited in the last 100 - 200 years. Although the technique has primarily been applied to lake sediments, at least one other study has used Pb-210 to determine sedimentation rates in a fluvial environment.[8] At this time the processes by which Pb-210 is deposited in fluvial sediments are not fully understood. Clearly the rate of sediment accumulation in a fluvial system is likely to be more variable than in a lacustrine one. Never the less, results from Pond Two indicate that in some fluvial environments there is justification for using the Pb-210 dating technique.

Samples from five cores (HM-2, MS-1, ML-1, KS-1, and BL-1) were submitted for isotope analysis for the purpose of determining sediment accumulation rates. For most of the cores the technique did not yield very satisfactory results. In most cases only a few of the upper sections had Po-210 levels significantly above background suggesting very low sedimentation rates and making it impossible to calcutate sediment accumulation rates from the isotope data . Only one core, HM-2 from Pond Two, yielded any meaningful results.

Core HM-2

Background levels of the isotope were not encountered in this core, however, if a background level of 1 DPM/g dry weight is assumed then the data suggest that the sediment accumulation rate in core HM-2 has varied between 1.0 amd 1.7 cm/yr (see Fig 5). The profile has been divided into three discrete segments over which constant sedimentation rates are assumed. In the upper portion of the profile the line of best fit through the data yields a sedimentation rate of 1.0 cm/yr for a period of approximately 32 years. Between 35 and 60 cm there is a zone of relatively constant Po-210 activity indicating the possibility of sediment mixing or extremely rapid sedimentation. The stratigraphic position of this section suggests that it is related to the Hurricane Hazel flood of 1954. The thickness of this section supports the suggestion that additional sediment was deposited on top of the 4 cm sand layer during receeding flow and that the 30-year sedimentation rates are maximum possible rates. The two linear segments below the discontinuity yield sedimentation rates of 1.7 cm/yr between 60 and 100 cm (approximately 1954 to 1930 AD) and 1.1 cm/yr between 100 and 148 cm (approximately 1930 to 1886 AD). The reason for the break in slope at 100 cm is not clear, although a sharp peak in Ambrosia percentage also occurs at this level. The average sedimentation rate for the entire analysed portion of the core is 1.4 cm/yr.

For the remaining cores it is essentially impossible to estimate sediment accumulation rates from Po-210 because there are too few data

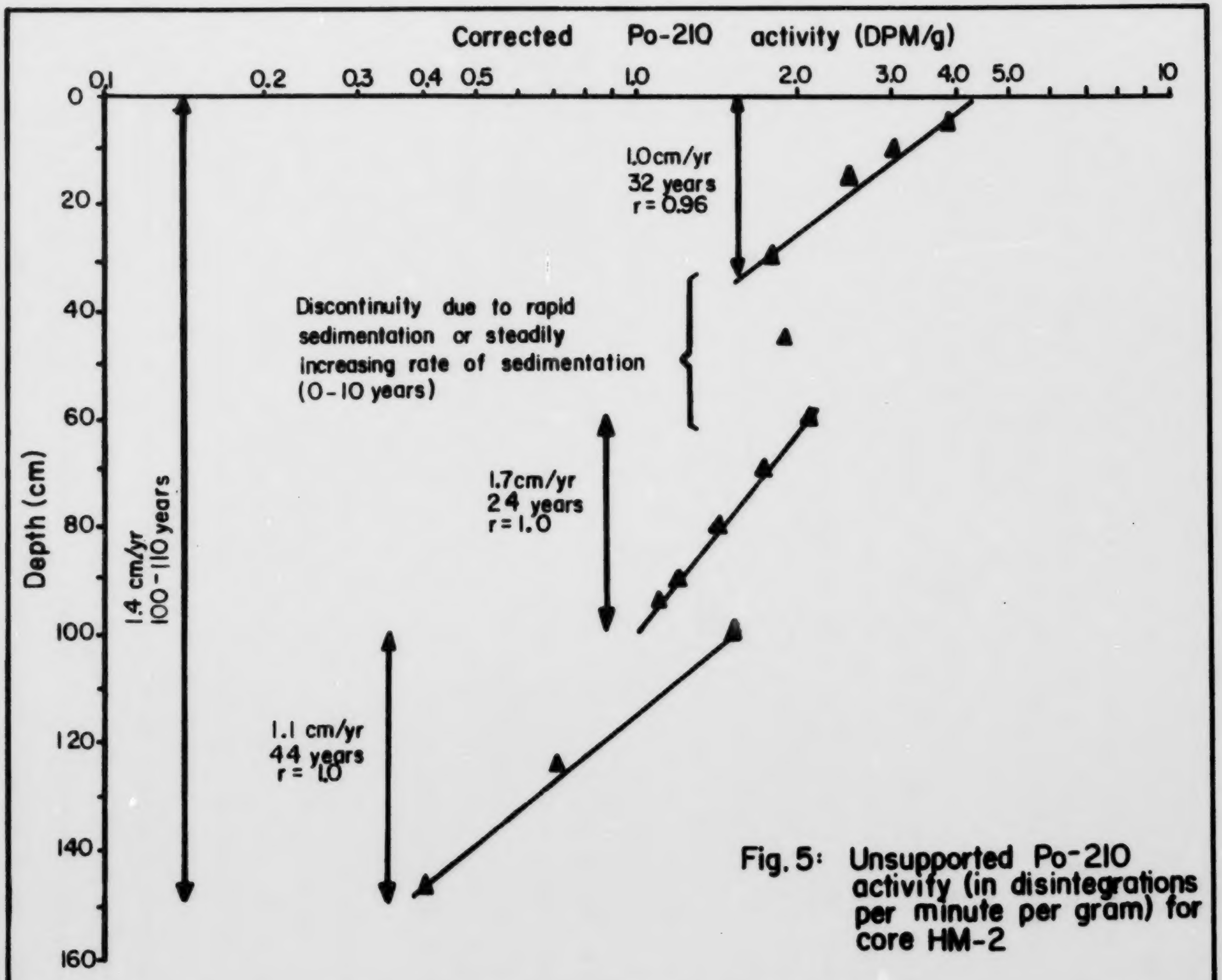

Fig. 5: Unsupported Po-210 activity (in disintegrations per minute per gram) for core HM-2

points above background. It is possible, however, to estimate sediment accumulation in these cores from the stable lead data obtained from the trace metal analysis. Previous studies[9] indicate that the concentration of anthropogenic lead in sediments started increasing significantly betwen 1850 and 1870 AD in northeastern North America in response to the burning of coal (since the 1920's the use of leaded gasoline has also contributed to atmospheric lead fallout). This marked increase in lead concentration appears to be a useable marker for the determination of mean sediment accumulation rates over the past 124 years. A visual scan of stable lead values in the cores (see Appendix B-2) suggests that background levels of stable lead in the Humber Marsh are close to 18 ug/g. This value agrees with regional background values for lead in the Great Lakes area. Thus, as would be expected from the preceeding discussion, the stable lead concentration (50 ug/g) reached in the deepest section of core HM-1 is above background and the sediments are younger than 1860.

Core MS-1

Examination of the stable lead profile suggests that background levels have been reached in the deepest section (89-91) of core MS-1. Ninety centimeters of deposition in 124 years yields an average sedimentation rate of 0.7 cm/yr. This rate is close to the 30-year sedimentation rate of 0.9 cm/yr.

Core KS-1

In core KS-1, stable lead concentration appears to have reached background at, or below, 68-70 cm resulting in an average sedimentation rate of 69 cm over 124 years, or 0.6 cm/yr. The 30-year sedimentation rate based on the presence of the sand layer is nearly three times as high (see Table 2). Such a high sedimentation rate in the past 30-years can be partly explained if more than 1 cm of material was deposited during the Hurricane Hazel flood.

Core ML-1

The stable lead profile suggests that background background levels have been reached in the deepest sections (69-71 cm) of core. If this depth corresponds to the 1860 marker for stable lead then the average sedimentation rate would to be 0.6 cm/yr. The latter value is three times greater than the 30-year sedimentation rate. The difference between these values may be related to the thickness of the sand layer found in this core. If the 22 cm of sand are not included in the stable lead concentration (this is justified because the sand is assumed to have been deposited instantaneously) then the resulting sedimentation rate is (70 - 22)cm/124 yrs = 0.4 cm/yr.

Core BL-1

Stable lead concentrations appear to have been reached at a shallow depth in core BL-1, possibly as low as 8-10 cm. This depth would yield a sedimentation rate of less than 0.1 cm/yr. This result disagrees with both the stratigraphic interpretation and the results of the analysis for organic pollutants (see section 5.2.2). If the sand layer between 8 and 17 cm is attributed to Hurricane Hazel (1954) a depth of 9 cm could not possibly correspond to 1860. According to the analysis, both PCB's and pesticides occur below 9 cm suggesting that the depth to background is 46-48 cm, resulting in an average sedimentation rate of 0.4 cm/yr. It is possible that low lead (and other metal) concentrations are an artifact of grainsize.

5.2 Pollutant Analysis

Fifty-seven sediment samples were analysed for the trace metals Cd, Cr, Cu, Mn, Ni and Pb. Fifty-six samples were analysed for the presence of PCB's, DDT, DDD, and DDE (see Appendix A). Replicate analysis were not performed (except for metals in one sample) hence the reliability of the concentration data (ie. confidence limits) could not be assessed. The Ontario MOE has established guidelines to determine whether contamination of sediments has taken place.[10] These guidelines were designed in order for the MOE to assess the suitability of dredgate spoils for open water disposal. The guidelines have been applied here to give an indication of sediment quality in the Humber Marsh. A list of sediment parameters and their abbreviations, detection limits, and MOE guidelines for dredgate are listed in Appendix A. Results of the pollutant analyses can be found in Appendices B-2 and B-3.

5.2.1 Trace Metal Accumulation

Sediments are a major storage compartment in fluvial systems for specific trace metals and other toxic substances. In this study, six trace metals (which by definition are normally present in sediment at low concentrations) were tested for. Duplicates of one sample were submitted from core HM-1 (46-48 cm). Comparison of the results suggests that concentration differences among samples on the order of those that occur between the duplicate samples cannot be considered significant. Results refer to total metal concentrations and no attempt was made to identify particular metal species.

Table 3 is a summary of trace metal concentrations in the sediments sampled. Mean concentrations of all elements where highest in core HM-1. Samples from core HM-1 also contained the highest concentrations of all elements except Mn. The lowest mean concentrations for all the elements were found in core HC-1.

MOE guidelines for metals in dredgate material suitable for open water disposal provide a guideline for assessing Humber Marsh sediment quality.

Cadmium (1.0 ug/g)

Twenty-one percent of the samples (12) had cadmium values greater than

Table 3: Summary of Trace Metal Concentrations in Sediment Cores from the Humber Marsh (all units are ug/g based on sediment dry weight).

Element	Cd (1.0)*		Cr (25)		Cu (25)		Mn		Ni (25)		Pb (50)	
Core	Range	Avg	Range	Avg	Range	Avg	Range	Avg	Range	Avg	Range	Avg
ML-1	<0.5-1.5	<1.1	41-64	58	29-43	38	560-690	597	26-40	34	18-105	63
MS-1	<0.5-1.5	<0.9	39-72	58	23-42	35	650-780	726	21-43	34	18-110	56
BL-1	<0.5-2.5	<0.7	31-80	59	17-56	37	440-970	656	19-47	35	16-150	47
KS-1	<0.5-1	<0.6	53-79	68	36-59	46	660 900	780	34-42	39	22-160	78
HM-1	<0.5-7	<2.4	60-108	86	43-79	64	750-940	815	42-85	54	50-190	118
HC-1	<0.5	<0.5	30-48	42	10-31	22	420-640	534	17-30	25	12-41	18
HC-2	<0.5-1.5	<0.6	41-69	50	20-33	27	510-830	650	21-29	26	14-71	38

* 1976 MOE Objectives

the MOE guideline. Five exceedences occurred in the seven samples from core HM-1.

Chromium (25 ug/g)
All samples tested exceeded the guideline for chromium.

Copper (25 ug/g)
Seventy-nine percent of the samples (45) exceeded the guideline for copper. Most of the samples which did not exceed the guideline were from cores taken from the channel area (HC-1 and HC-2).

Manganese (no MOE objective available)
According to U.S. Environmental Protection Agency (EPA) criteria, sediments containing > 500 ug/g Manganese are heavily polluted. Fifty-three of the samples (93 %) analysed for Mn were above this limit. According to Thomas and Mudroch [11] the background level of manganese in the bluffs surrounding Lake Ontario is approximately 929 ug/g. Only two of the 57 samples analysed had manganese levels greater than this local background level.

Nickel (25 ug/g)
Eighty-six percent of the samples (49) had nickel values greater than the guideline. Of the eight samples which were below the guideline six were from the channel cores.

Lead (50 ug/g)
Fourty-six percent of the samples (26) exceeded the guideline for lead. All samples taken from core HM-1 had lead concentrations which were greater than or equal to the MOE guideline.

Most elements showed no systematic change in concentration with depth (see Fig 6). The concentrations vary but do so erratically, possibly reflecting grain-size differences between samples, or variations in organic matter and/or metal (Fe, Mn) oxide coatings. Lead is the exception, all of the cores exhibit decreasing lead concentration with depth. The results from the one duplicate sample (core HM-1, 46-48

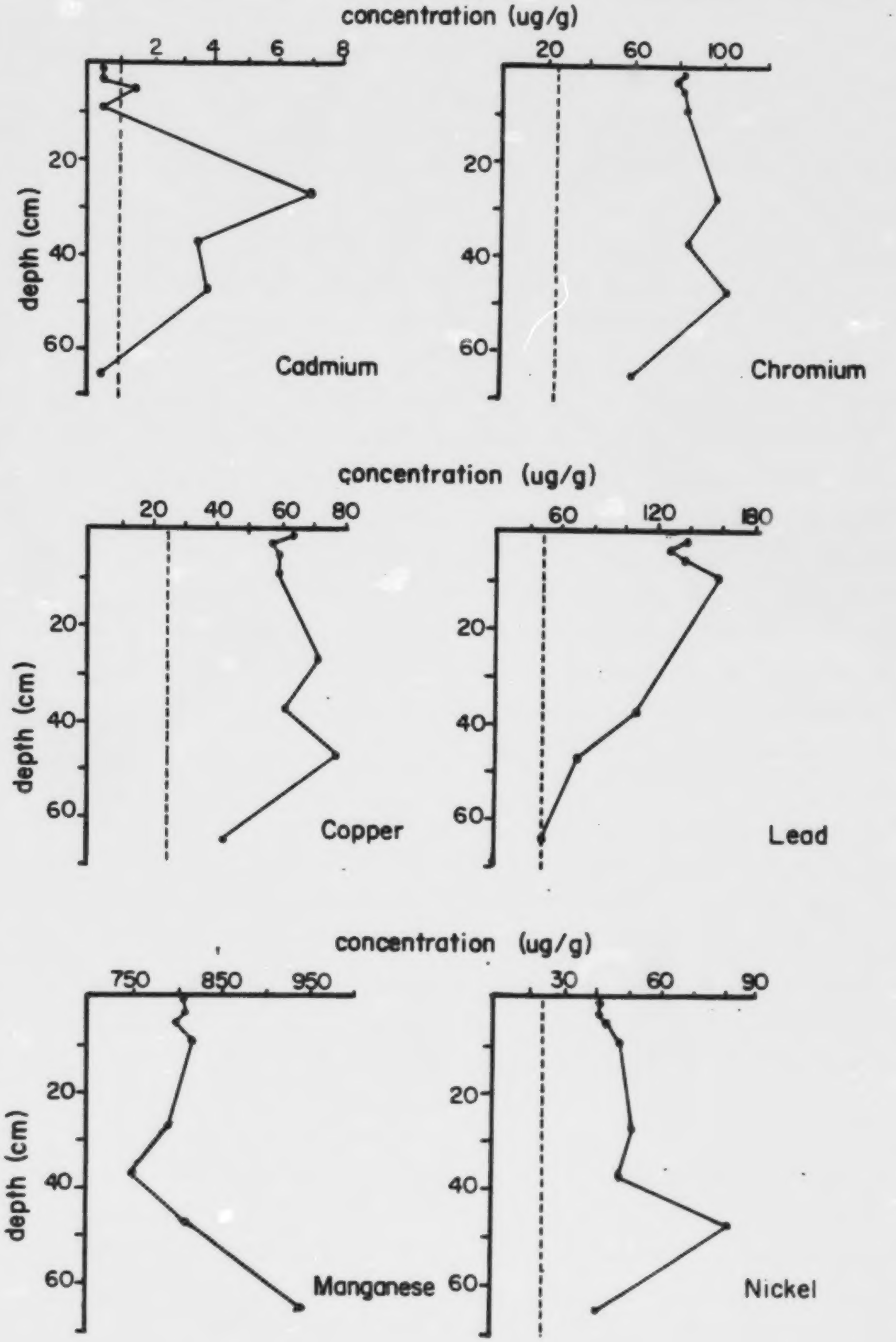

Fig. 6: Trace metal concentrations in a sediment core (HM-1) from the Humber Marsh (note scale changes, dotted lines are MOE guidelines).

cm) suggest that concentration differences on the order of 0.5 ug/g for cadmium, 1 ug/g for copper, 2 ug/g for lead, 4 ug/g for nickel, 10 ug/g for chromium and 20 ug/g for manganese should not be considered significant.

Analysis of sediment cores can provide information on anthropogenically related trace metal accumulation. However, before determining if enrichment has occurred, background levels of the metals in question must be established for the environment under study. In cores with low lead concentrations at depth (ie. $\leqslant$ 18 ug/g) it is probable that concentrations of other metals are also close to background. Cadmium, chromium, copper, manganese and nickel concentrations do not appear to vary significantly between the surface and the deepest sections analysed suggesting that little, if any, anthropogenic enrichment of these metals has occurred. This result was unexpected considering the urbanized nature of the Humber watershed. An increase in sediment caliber as a result of urban development in the watershed may partly explain the absence of expected increases in sediment pollutant concentration.

Background levels of lead were not reached in core HM-1 (Pond Two), as was to be expected based on the high sedimentation rate calculated for this site; however, comparison of metal concentrations in this core with those in neigboring cores indicates cadmium enrichment between 26 and 48 cms, as well as some chromium, copper and nickel enrichment. One possible explanation for the higher metal concentrations in this core is presented in section 5.2.2 below.

5.2.2 PCB Accumulation

Polychlorinated biphenyls (PCB's) are a group of toxic chlorinated organic chemicals which are highly resistant to degradation. The chemical stability of PCB's allows them to persist and accumulate in the environment. PCB's tend to adsorb onto particulate matter and hence in the aquatic environment they preferentially accumulate with fine-grained sediments. PCB's were used extensively in Canada for at least forty years before their use was restricted in 1977 under the Environmental Contaminants Act.

Sediments from the Humber Marsh were analysed for PCB content (see Table 4 for a summary of data). The MOE guideline for PCB's in dredgate soil is 50 ng/g. PCB concentrations in Humber Marsh samples ranged from below detection limit (10 ng/g) to 164 ng/g. The MOE guideline for dredgate was exceeded in 36% of the samples (20) analysed. No PCB's were detected in 20% of the samples.

The highest concentrations of PCB's were found in core HM-1 from Pond Two (average 98.5 ng/g); seven out of eight samples from this core exceeded the Ministry guideline. The lowest concentrations occurred in core HC-1 (average 13.5 ng/g) from the channel. The difference in PCB concentrations between these two cores can be partly attributed to the coarser nature of the sediments in the channel. Thus, in addition to having elevated metal concentrations, core HM-1 has an average PCB concentration more than two times greater that of any other core. Factors, other than grain size, may help to explain the variation. The proximity of Pond Two to the main channel may also be a significant factor in causing elevated pollutant concentrations. Water, suspended sediment and associated pollutants are able to pass more easily from the channel into Pond Two than into other ponds during high flow events. As a result Pond Two could receive a larger portion of polluted sediments than ponds farther upstream.

An earlier TAWMS study identified two dry weather outfalls that empty directly into Marsh Two.[12] In addition to storm flow from rainfall events, these outfalls also convey flow from unknown sources and thus they may represent a localized source of pollutants. Another process that may further influence sediment and pollutant accumulation is the backup of water into Pond Two during storm events on Lake Ontario (ie. seiches) or during times of high water levels in Lake Ontario.

Table 4: Summary of PCB concentrations in Sediment Cores from the Humber Marsh (all units are in ng/g).

Environment	Core	Min.	Max.	Avg.[a]	Surf. Conc.
Pond	HM-1	12.4	163.4	98.5	68.9
	MS-1	<10	76.6	32.6	56.6
	KS-1	<10	139.8	47.2	58.6
Levee	ML-1	<10	60.0	39.5	52.7
	BL-1	<10	133.8	39.6	57.1
Channel	HC-1	<10	29.0	13.5	29.0
	HC-2	<10	78.8	25.2	32.3
Summary		<10	163.8	42.3	

[a] Computed with <10 = 10

High PCB concentrations occurred less than 10 cm below the surface in cores taken from the ponds and levees (see Fig 7). Three cores (MS-1, KS-1, and HM-1) exhibited peaks in PCB concentration in sediment that was probably deposited around 1980. However, because of the shallow depths being considered and the uncertainties encountered in determining recent sedimentation rates, these peaks in PCB concentration cannot be accurately dated. The decline in PCB concentration near the surface may be a reflection of decreased PCB input due to restrictions imposed on their use since 1977, but more data are needed to validate this trend. In two cores (ML-1 and BL-1) the highest PCB concentrations occurred in the deepest sections analysed. It is not known why such high PCB concentrations were found at this depth (ie. > 60 cm).

PCB concentrations in sediment cores taken from the channel area were comparable to, or less than, concentrations of the same compound in cores from the ponds and levees. Any differences probably reflect

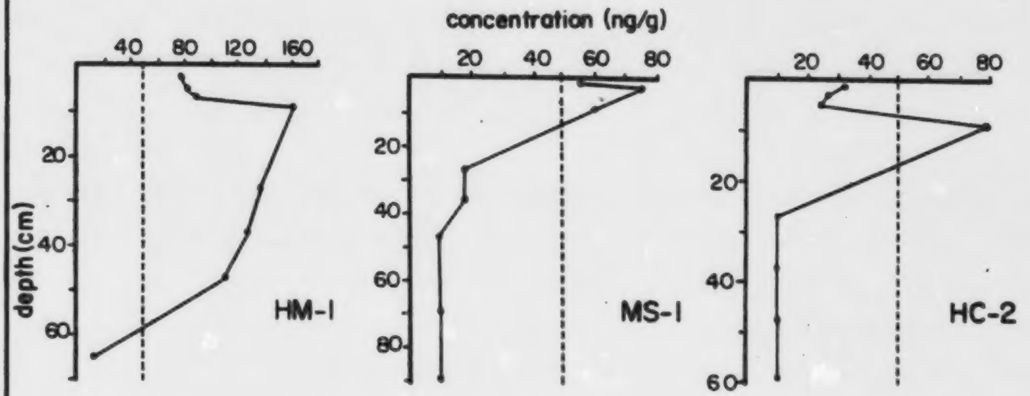

Fig. 7: PCB concentrations in three sediment cores from the Humber Marsh (note scale differences, dotted lines are MOE guidelines).

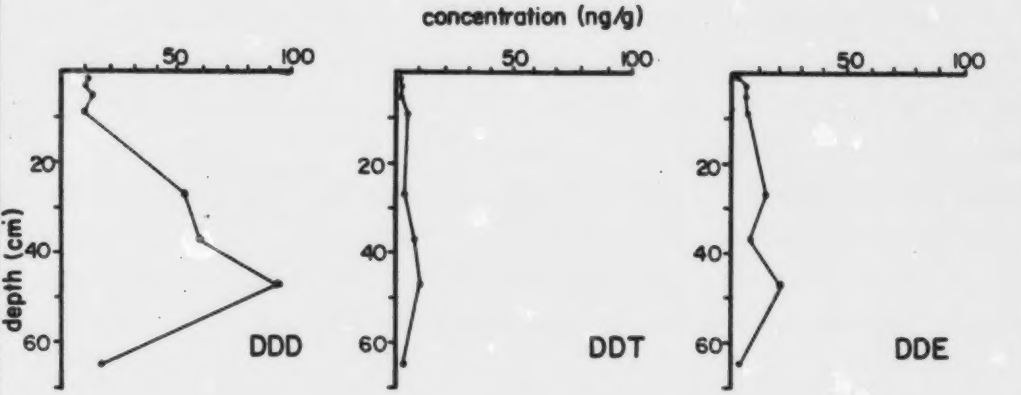

Fig. 8: DDD, DDT and DDE concentrations in a sediment core (HM-I) from the Humber Marsh.

grain size variations between the channel and adjacent environments. However, since PCB's have a higher affinity for organic rich suspended solids than sand or silt most of the PCB's in the Humber River are probably being transported in suspension downstream to Lake Ontario.

For comparison, two surface bed-sediment samples taken from Black Creek and the Humber River in 1981 had PCB concentrations of 50 and 360 ng/g, respectively.[13] Both values are similar to surface concentrations found in this study. The highest PCB concentrations found in the Humber River Marsh were several orders of magnitude less than the maximum total PCB concentrations found in the bottom sediments of the Niagara River.[14]

5.2.3 Pesticide Accumulation

DDT was first used in Ontario in 1943[15] and was used widely until 1954. In 1954 the first government legislation was passed to control the use of both DDT and DDD in Ontario. Further legislation was passed in 1956, 1957, 1961, 1963 and 1964. By 1967 the Ontario Water Resources Commisson stopped issuing permits for the use of DDT in water and the Department of Lands and Forests discontinued the use of DDT entirely in all its spraying programs. DDT is now rarely used in Ontario, however it has not yet been entirely banned.

DDT and its metabolites (breakdown products) DDD and DDE, like PCB's and other chlorinated hydrocarbons, are insoluble in water, resistant to degradation and tend to accumulate and persist in aquatic environments.

Results of the analysis for DDT, DDD and DDE are listed in Appendix B-4 and summarized in Table 5. There are no MOE guidelines for pesticide in aquatic sediments. Peaks in pesticide concentration commonly occur just above or below the sand layer attributed to Hurricane Hazel (approx. 1954) (see Fig. 8) when DDT was still widely used. Declining pesticide concentrations near the surface may be a

Table 5: Summary of Pesticide Concentrations in Sediment Cores from the Humber Marsh (all units are in ng/g).

Core		Parameter	Min.	Max.	Avg.[a]	Surf. Conc.
Pond	HM-1	DDT	<1	7.5	3.0	1.5
		DDD	9.7	93.9	34.3	12.8
		DDE	<1	21.3	8.3	<1
	MS-1	DDT	<1	38.0	6.0	1.6
		DDD	<1	35.1	15.6	13.8
		DDE	<1	6.7	3.4	4.0
	KS-1	DDT	<1	11.3	3.7	9.9
		DDD	<1	38.2	17.2	19.1
		DDE	<1	12.0	5.5	5.5
Levee	ML-1	DDT	<1	10.7	3.4	3.5
		DDD	<1	52.9	22.5	17.9
		DDE	<1	16.0	5.7	6.7
	BL-1	DDT	<1	< 1	< 1	< 1
		DDD	<1	44.8	13.2	25.4
		DDE	<1	13.3	5.3	12.0
Channel	HC-1	DDT	<1	5.0	1.7	4.5
		DDD	<1	6.7	1.9	7.2
		DDE	<1	10.7	2.2	18.7
	HC-2	DDT	<1	65.0	10.1	5.0
		DDD	<1	70.4	12.4	6.7
		DDE	<1	18.7	5.1	10.7
Summary		DDT	<1	65.0	4.1	-
		DDD	<1	93.9	15.7	-
		DDE	<1	21.3	5.1	-

[a] Computed with <1 ng/g = 1 ng/g

reflection of legislation passed in 1967 which virtually banned the use of DDT. Nevertheless, the continued presence of DDT in surface samples is surprising since it is unlikely that there have been any significant inputs of DDT into the Humber watershed since 1967 (unexpectedly high concentrations of DDT were also found in Niagara River sediments[14]). The persistence of DDT is well documented however and its presence in surface sediments from the Humber Marsh may be related to the inwash of previously contaminated soil particles.

DDT concentrations are generally lower than DDD or DDE concentrations presumably since DDT is broken down to its more persistent isomers, DDD and DDE. Relatively low concentrations of DDT compared to its metabolites suggests that little DDT is of recent origin. DDD is the anaerobic breakdown product of DDT and it is the most frequently occurring isomer in the Marsh environment.

No DDT was detected in core BL-1; however its decomposition products DDD and DDE were present. The highest concentrations of DDD and DDE were found in core HM-1 from Pond Two. Surprisingly, the highest concentration of DDT (65 ng/g) was found in the channel sediments (core HC-2) between 8-10 cm. This finding is reinforced by high DDD versus DDE values (DDE is the more stable isomer and hence would be expected to occur in higher concentrations if no new DDT has been added to the system). These findings may reflect recent use of products containing DDT in the Humber River watershed; however, the surface samples of both cores showed higher DDE values as would be expected in older material.

A recent study dealing with toxic contaminants in the Niagara River reports DDT, DDD, and DDE concentrations in Niagara River bottom sediments ranging from below detection limit (<1 ng/g) to 73, 54, and 280 ng/g, respectively[14]. DDT and DDD concentrations are compareable in Humber Marsh and Niagara River sediments. However, the DDE concentrations found in the Humber Marsh sediments are an order of magnitude lower than those found in the Niagara River sediments.

5.3 Pollutant Mass Balance in Humber River Marsh Sediments

The mass of specific pollutants stored in Humber Marsh sediments can estimated from the core data. In this study, only mass estimates for Pb, PCBs and pesticide (DDT, DDD and DDE) were made. Estimates are not given for other trace metals because it could not be firmly established that surface concentrations were sigificantly greater than local background levels. Although metal concentrations (particularly Cd) are elevated in core HM-2, additional cores from the same area would be required to estimate the mass of anthropogenically derived trace metals in this localized area.

In order to estimate the mass of PCBs, pesticide and Pb stored in the Marsh sediments the following equation was used:

$$\text{Pollutant Mass} = \overline{P} * \overline{W} * \frac{A_m}{A_c} * \frac{L_c}{L_s} \qquad (1)$$[*]

where $\overline{P}$ is the average pollutant concentration (kg/g)[**] in the core(s), $\overline{W}$ is the average weight of sediment (g) in a sampling interval, A_m is the sedimentation area (cm^2), A_c is the area (cm^2) of the sampling tube, L_c is the average length (cm) of cores used in calculation, L_s is the length of the sampling interval (cm). For a given sedimentary environment results are averaged over the length of a core and the number of cores taken. Although loss of accuracy results, it must be pointed out that this is only a crude calculation. The major drawbacks in the estimation are the lack of continuous data throughout the length of each core and the failure of the cores to penetate deep enough to eliminate any anthropogenic influence. The estimate does not include contaminants adsorbed onto sediment suspended in the water column.

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[*] adapted from Oliver, 1984a

[**] for lead, P is the average Pb concentration > 18 ug/g.

The approximate masses of PCBs, pesticide and Pb stored in the sedimentary environments shown in Fig. 2 are listed in Table 6 below. They are at best however only order of magnitude estimates. The largest volume of Pb, PCB's, DDE and DDD is associated with the backwater ponds. The largest volume of DDT is associated with the channel sediments.

Table 6: Mass of Selected Pollutants in Humber Marsh Sediments.

Sedimentary Environment	Area (m^2) (A_m)	Pollutant Masses (kg) PCB's	DDE	DDD ($\overline{P}$)	DDT	Pb
Backwater Ponds	120,000	1.5	0.14	0.57	0.11	1700
Levee-Floodplain	130,000	1.0	0.14	0.44	0.05	900
Channel	120,000	0.7	0.14	0.26	0.22	400
Totals	370,000	3.2	0.42	1.27	0.38	3000

Data used to estimate the masses of selected pollutants stored in the Humber Marsh sediments is listed in Appendix B-5.

6. Summary and Conclusions

Pollen, radiochemical and stratigraphic analyses indicate that sediments are actively accumulating in the Humber River Marsh. Rates of sediment accumulation are greatest in the backwater ponds. Of the three backwater ponds investigated the pond closest to Lake Ontario (Pond Two) had the highest sedimentation rate. Since urban development in the Humber River watershed has now subsided, future sedimentation rates will probably be lower than those calculated for the past 30 - 124 years.

Contaminated sediments have been accumulating in the backwater ponds and on the levees for at least the past 30 years. This trend will probably continue as long as water quality remains unchanged and these areas continue to receive sediment. The Humber Marsh is a popular recreational area and valuable wildlife habitat; the presence of pollutants in the sediments may be incompatible with these uses. In the channel, contaminated sediments may accumulate temporarily (ie. seasonally) before being transported downstream to Lake Ontario where they probably accumulate in the sediments of Humber Bay.

In general, the metal concentrations found in the Marsh were low (probably close to background levels); cadmium and lead were exceptions. Cadmium concentrations were elevated in Pond Two. Lead concentrations were elevated in the surface sediments of all cores. Ontario Ministry of the Environment guidelines for metals in dredgate material suitable for open water disposal were frequently exceeded.

PCB's and pesticide were found in nearly all the cores analysed. The Ontario Ministry of the Environment guideline for PCB's in dredgate material was exceeded in about one third of the samples. In most cores, PCB and pesticide concentrations declined near the surface. DDT was found in surface sediments possibly indicating recent addition of this compound to the watershed.

The consistently low concentrations of most pollutants in the channel area is related to sediment texture and to the fact that fine sediments tend to be associated with organic matter which readily adsorbs both metal and organic contaminants. Thus, sandy sediments are likely to contain lower levels of pollutants than finer sediments. Two additional factors may explain the higher pollutant concentrations and higher sedimentation rates found in Ponds Two. First, chronic flow from two dry weather outfalls bordering the site may be a localized source of pollutants. Second, the proximity of the site to the channel and to Lake Ontario enables water, suspended sediment and associated pollutants to enter the pond during high flow events and at times of high lake level.

Results from this study are relevant to future studies of this type and to those interested in monitoring sediment and pollutant accumulation in urban rivers. First, coarser channel sediments may remain relatively clean while nearby zones where fine-grained sediments accumulate may become polluted. As a result, samples taken from the channel areas may not be indicative of local sediment quality. Second, since sediment deposited during and after urbanization is often coarser than previously deposited material, variations in sediment pollutant concentration with depth may not reflect changing water quality over time unless grainsize effects are removed. Third, the use of regionally established background levels for metals as an indication of local sediment quality may not always be appropriate because natural metal concentrations may vary considerably among different environments. In this study for example, concentrations of Cr, Cu, Mn, and Ni exceeded MOE guidelines for dredgate even though surface concentrations of these metals did not differ significantly from those at depth (ie. background level), even in the cores with the lowest sedimentation rates. Fourth, because local sedimentation rates may vary considerably it is important to investigate sedimentation rates before designing a sampling program. This will insure that metal background levels are reached and that appropriate sampling intervals are chosen. Sampling can then proceed in the most focused manner and analytical expenses can be reduced. In the Humber Marsh backwater ponds for example, preliminary knowledge of historical sedimentation rates could have been obtained from palynological analysis.

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Appendices

Appendix A: List of Study Compounds and their Abbreviations, Detection Limits and MOE Objectives

Compound	Abbreviation	Detection Limit (ug/g)	MOE Objective (ug/g)
Cadmium	Cd	0.5	1.0
Chromium	Cr	1	25
Copper	Cu	1	25
Manganese	Mn	2	NA
Nickel	Ni	2	25
Lead	Pb	2	50
		(ng/g)	(ng/g)
Polychlorinated biphenyls	PCB's	10	50
1,1,1-trichloro-2,2-bis (4-chlorophenyl)-ethane	4,4-DDT	1	NA
1,1-dichloro-2,2-bis(4-chlorophehyl)-ethylene	4,4-DDE	1	NA
1,1-dichloro-2,2-bis(4-chlorophenyl)-ethane	4,4-DDD	1	NA
Polonium	Po		
Radium	Ra		
Radon	Rn		

Appendix B-1: Results of Po-210 analysis for core HM-2

Depth (cm)	Supported Po-210 Specific Activity DPM/g	Error in Po-210 Specific Activity (1 sigma) DPM/g
0-2	3.8	0.4
5-7	4.9	0.4
10-12	4.1	0.4
15-17	3.5	0.4
30-32	2.8	0.4
45-47	2.9	0.4
60-62	3.1	0.4
70-72	2.7	0.4
80-82	2.4	0.4
90-92	2.2	0.4
94-96	2.1	0.4
100-102	2.5	0.4
125-126	1.7	0.2
147-148	1.4	0.2

DPM/g = disintegrations per minute per gram

Appendix B-2: Complete Results of Metal Analysis (unspecified units are ug/g).

Core	Depth (cm)	Cd R=83% MDL=0.5	Cr R=96% MDL= 1	Cu R=105% MDL= 1	Mn R=102% MDL= 2	Ni R=112% MDL= 2	Pb R=102% MDL= 2
ML-1	0-2	1.0	64	42	620	36	104
	3-5	1.0	59	42	590	35	105
	7-9	1.5	64	43	560	37	100
	12-14	1.5	59	40	600	33	77
	18-20	0.5	41	29	560	26	38
	34-36	1.5	54	39	690	34	46
	52-54	<0.5	64	36	560	40	29
	69-71	1.0	56	30	600	34	18
MS-1	0-2	1.0	64	42	780	38	95
	2-4	1.5	59	38	750	35	86
	8-10	1.5	63	41	740	37	110
	26-28	1.0	39	23	650	21	35
	35-37	<0.5	50	31	680	29	42
	46-48	1.0	72	39	750	43	43
	68-70	<0.5	64	33	700	40	22
	89-91	<0.5	50	29	760	32	18
KS-1	0-2	<0.5	75	59	740	34	120
	2-4	1.0	79	49	690	35	110
	8-10	<0.5	73	50	790	40	160
	26-28	<0.5	53	39	890	38	56
	36-38	<0.5	65	48	840	42	70
	46-48	<0.5	64	47	790	40	49
	58-60	<0.5	69	39	600	41	38
	68-70	<0.5	66	36	900	40	22
BL-1	0-2	<0.5	66	46	610	33	110
	2-4	2.5	72	56	580	47	150
	8-10	<0.5	31	17	480	19	24
	26-28	<0.5	52	28	660	31	20
	36-38	<0.5	80	38	800	39	21
	46-48	<0.5	60	34	970	38	18
	58-60	<0.5	56	34	710	35	16
	68-70	<0.5	56	43	440	38	18
HM-1	0-2	<0.5	83	64	810	43	140
	2-4	<0.5	80	58	810	43	130
	4-6	1.5	83	60	800	45	140
	8-10	<0.5	84	60	820	49	160
	26-28	7	98	72	790	53	190
	36-38	3.5	85	62	750	49	110
	46-48	4	98	78	800	81	74
	46-48	3.5	108	79	820	85	72
	64-66	<0.5	60	43	940	42	50

Appendix B-2 cont.

Core	Depth (cm)	Cd R=83% MDL=0.5	Cr R=96% MDL= 1	Cu R=105% MDL= 1	Mn R=102% MDL= 2	Ni R=112% MDL= 2	Pb R=102% MDL= 2
HC-1	0-2	<0.5	40	21	640	21	41
	2-4	<0.5	30	10	550	17	20
	6-8	<0.5	38	24	480	23	14
	8-10	<0.5	44	23	550	28	16
	12-14	<0.5	40	31	420	25	14
	26-28	<0.5	47	22	560	29	14
	28-30	<0.5	46	25	530	31	15
	38-40	<0.5	48	22	540	30	12
HC-2	0-2	<0.5	48	26	630	21	62
	2-4	<0.5	54	32	750	26	54
	4-6	<0.5	48	30	700	26	71
	8-1	1.5	52	33	830	29	62
	26-2	<0.5	46	27	510	29	14
	36-3	<0.5	69	25	530	28	14
	46-4	<0.5	41	20	650	24	14
	58-6	<0.5	42	20	600	26	14

R = percent recovery
MDL = method detection limit

Appendix B-3: Complete Results of Analysis for PCB's and Pesticides (unspecified units are ng/g)

Core	Sediment Interval (cm)	Total PCB R=82% MDL=10	4,4-DDE R=85% MDL= 1	4,4-DDD R=90% MDL= 1	4,4-DDT R=92% MDL= 1
ML-1	0-2	52.7	6.7	17.9	3.5
	3-5	46.1	6.7	14.6	3.4
	7-9	60.7	4.0	52.9	10.7
	12-14	30.2	16.0	48.2	5.1
	18-20	16.5	3.3	9.6	1.1
	34-36	13.4	6.0	35.1	1.2
	52-54	< 10	< 1	< 1	< 1
	69-71	86.5	1.5	< 1	< 1
MS-1	0-2	56.6	4.0	13.8	1.6
	2-4	76.6	6.7	13.2	38.0
	8-10	61.0	2.0	12.2	3.3
	26-28	18.4	4.7	28.0	< 1
	35-37	18.0	4.7	35.1	< 1
	46-48	< 10	2.7	19.2	< 1
	68-70	< 10	< 1	< 1	< 1
	89-91	10.2	1.3	2.3	< 1
KS-1	0-2	58.6	5.5	19.1	9.9
	2-4	69.5	5.8	17.9	11.3
	8-10	139.0	6.0	14.4	< 1
	26-28	24.3	4.7	38.2	3.6
	36-38	31.7	12.0	18.8	< 1
	46-48	34.6	7.8	25.0	< 1
	58-60	< 10	< 1	3.0	< 1
	68-70	< 10	< 1	< 1	< 1
BL-1	0-2	57.1	12.0	25.4	< 1
	2-4	76.2	13.3	44.8	< 1
	8-10	< 10	2.5	24.4	< 1
	26-28	< 10	8.7	6.0	< 1
	36-38	< 10	< 1	< 1	< 1
	46-48	< 10	< 1	< 1	< 1
	58-60	< 10	< 1	< 1	< 1
	68-70	133.8	3.1	1.7	< 1
HM-1	0-2	68.9	< 1	12.8	1.5
	2-4	79.6	6.0	11.9	2.2
	4-6	83.8	6.0	13.8	1.7
	8-10	163.4	6.7	9.7	4.5
	26-28	139.4	14.7	54.0	3.4
	36-38	128.5	8.0	60.4	7.5
	46-48	112.0	21.3	93.9	< 1
	64-66	12.4	3.3	17.8	2.4

Appendix B-3 cont.

Core	Sediment Interval (cm)	Total PCB R=82% MDL=10	4,4-DDE R=85% MDL= 1	4,4-DDD R=90% MDL= 1	4,4-DDT R=92% MDL= 1
HC-1	0-2	29.0	10.7	6.7	5.0
	2-4	10.0	< 1	2.7	2.7
	6-8	< 10	< 1	< 1	< 1
	8-10	< 10	< 1	< 1	< 1
	12-14	19.0	< 1	< 1	< 1
	26-28	< 10	< 1	< 1	< 1
	28-30	< 10	< 1	< 1	< 1
	38-40	< 10	< 1	< 1	< 1
HC-2	0-2	32.3	18.7	7.2	4.5
	2-4	26.6	3.3	7.7	4.9
	4-6	24.0	4.7	9.7	2.8
	8-10	78.8	8.0	70.4	65.0
	36-38	< 10	2.7	< 1	< 1
	46-48	< 10	< 1	< 1	< 1
	58-60	< 10	< 1	< 1	< 1
	68-70	< 10	< 1	< 1	< 1

R = percent recovery
MDL = method detection limit

Appendix B-5: Data Used to Estimate Mass of Pollutants Stored in Humber Marsh Sediments

Sedimentary Environment	Core	$\overline{P}$ (kg)					$\overline{W}$ (g)	A_c	L_c(cm)	L_s(cm)
		PCB's	DDE	DDD	DDT	Pb				
			(*10^{-12})			(*10^{-8})		(*$10^{-3}m^2$)		
backwater ponds	MS-1	33	3.4	15.6	6.0	3.8	8.2	1.7	91	2
	KS-1	47	5.5	17.2	3.7	6.0	9.4	1.7	78	2
	HM-1	99	8.3	34.3	3.0	10.0	9.4	1.7	72	2
	Ave.	60	5.7	22.4	4.2	6.6	9.0	1.7	80	2
levee-floodplain	ML-1	39	5.7	22.5	3.4	4.7	9.3	1.7	73	2
	BL-1	40	5.3	13.2	<1.0[a]	2.9	7.1	1.7	84	2
	Ave.	40	5.5	17.9	2.2	3.8	8.2	1.7	79	2
channel	HC-1	14	2.2	1.9	1.7	-----	18.7	1.7	40	2
	HC-2	25	5.1	12.4	10.1	2.0	21.9	1.7	64	2
	Ave.	19	3.7	7.1	5.9	1.0	20.3	1.7	52	2

[a] calculated with < 1 = 1

REGIONAL GEOCHEMICAL STRATIFICATION OF SHALLOW GROUNDWATERS RESULTING FROM CATCHMENT URBANIZATION

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Key words: Groundwater, Impact of Urbanization, Contaminant Migration.

ABSTRACT

Contact springs along the Scarborough Bluffs of eastern Metropolitan Toronto provide an ideal opportunity for studying the impact of urban development on shallow groundwater quality. Occupying 12 km of Lake Ontario shoreline, the Scarborough Bluffs represent an important discharge zone for a series of minor aquifers defined within the multi-layer sequence of tills, deltaic sands, and glacio-lacustrine diamicts. Within these deposits, a shallow aquifer system is recharged locally through areas which have recently been transformed from rural pasture to well populated commercial, industrial and residential areas. The deeper aquifer units form part of a regional flow system and are recharged primarily in rural parts of the extensive groundwater catchment.

A major ion, minor ion, trace metal and environmental isotope study of the spring waters reveals major differences in chemical character between the two systems. Groundwaters from the deeper aquifers are low in total dissolved solids and show many similarities to uncontaminated, low tritium and chemically mature waters from deep aquifers in the Duffin Creek-Rouge River drainage basins to the north and east of Metropolitan Toronto. By comparison, the shallow groundwaters reveal the effects of urban development and consistently display elevated concentrations of Ca, Na, NO_3 and Cl with average values of 155, 95, 35, and 200 mg/L respectively. These compare with average values of 70, 10, 5 and 10 mg/L respectively in the deeper waters.

Trace element concentrations of Cr, Co, Cd, Mo, Pb, Mn, Fe, Cu, Ni, Zn, Al and Hg in the spring waters exhibit considerable variability but several high anomalies are noted in the shallow, contaminated waters when compared to background levels determined in rural parts of the groundwater catchment. Since these elements may provide insight to contaminant source origin, complementary investigations are being conducted involving drilling and pore water extraction and analysis at sites where specific types of contamination are suspected. For example, vertical profiles of pore water chemistry from the unsaturated zone adjacent to major salted highways show Cl concentrations up to 14,000 mg/L and provide a range of diagnostic chemical criteria that can be used to confirm suspected road salt contamination in disputed situations.

REGIONAL GEOCHEMICAL STRATIFICATION OF SHALLOW GROUNDWATERS RESULTING FROM CATCHMENT URBANIZATION

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ABSTRACT

Occupying 12 km of Lake Ontario shoreline, the Scarborough Bluffs of eastern Metropolitan Toronto represent an important zone of groundwater spring discharge for a series of minor aquifers defined within the multi-layer sequence of tills, deltaic sands and glacio-lacustrine diamicts. Within these deposits a shallow aquifer system is recharged locally through areas which have been recently transformed from rural pasture to well populated commercial and residential areas. The deeper aquifer units form part of a regional flow system and are primarily recharged in rural parts of the groundwater catchment.

A major ion, minor ion and trace element study of the spring waters reveals pronounced differences in chemical character between the two systems. Groundwaters from the deeper aquifers tend to be low in total dissolved ion content and generally contain <50 mg/L Cl and <10mg/L NO_3. In contrast groundwaters from the shallow system exhibit the considerable effects of urbanization and contain concentrations of many inorganic constituents considerably above background concentrations determined for naturally evolving uncontaminated groundwaters in the Duffins Creek - Rouge River drainage basins to the north and east of Metropolitan Toronto. In many cases Cl and NO_3 concentrations exceed 500 mg/L and 30 mg/L respectively.

Detailed site studies involving drilling and comprehensive inorganic chemical analysis of vertically migrating pore waters are being conducted to investigate the extent of the contamination and to evaluate the potential use of minor ions and various trace metals as diagnostic indicators of contaminant source origin. Most of the early work has focused on groundwater contamination by road de-icing chemicals and vertical profiles of pore water chemistry from the unsaturated zone adjacent to major salted highways show chloride concentrations up to 14000 mg/L. There are also indications from these studies that low I/Cl ratios together with the enhanced presence of certain trace elements may be useful in distinguishing road salts from other sources of chloride enrichment.

INTRODUCTION

Urbanization is an important example of a non-point contaminant source that has received little attention as far as groundwater resources are concerned. Urbanization results in the production of large volumes of surface water run-off which can accumulate significant concentrations of organic and inorganic dissolved material. These waters can subsequently recharge aquifers in more permeable areas of the catchment and water quality degradation eventually results. The problem is seriously compounded in many parts of Canada where road de-icing chemicals are extensively applied during winter months.

A study is currently in progress which has the ultimate aim of understanding the distribution, origins and behaviour of local shallow groundwaters containing elevated concentrations of chloride. Since urbanization is believed to be an important potential source of chloride, the initial studies described in this paper are focusing on the contribution of urban activities to low level, inorganic contamination of shallow groundwaters. The primary objectives of these initial studies are:

i) to determine the extent to which non-point source contaminants such as road de-icing chemicals and products of urban development are accumulating in the shallow sub-surface environment;
ii) to determine the migration rates and chemical behaviour of the contaminants, and
iii) to identify inorganic chemical parameters that could be used to isolate the source of contamination.

GENERAL APPROACH

The problem has been approached using a three-stage process:

i) to determine natural background levels of major, minor and trace inorganic constituents in naturally evolving uncontaminated groundwaters;
ii) to document the inorganic geochemical character of groundwaters in aquifers underlying urbanized areas and adjacent to major salted highways; and
iii) to investigate, in detail, at carefully selected urban and roadside sites, the inorganic geochemistry of recharge waters as they migrate through the unsaturated zone.

As shown on Figure 1 the various elements of the study have been conducted in range of localities. Regional hydrochemical investigations have been undertaken in the Duffins Creek - Rouge River Drainage Basins (1), Ops township near Lindsay (2), and the Scarborough Bluffs (3). Hydrochemical studies of recharge waters from the unsaturated zone have so far been centred on sites along the Don Valley Parkway (4), at Ballantrae (5) and at Milliken (6).

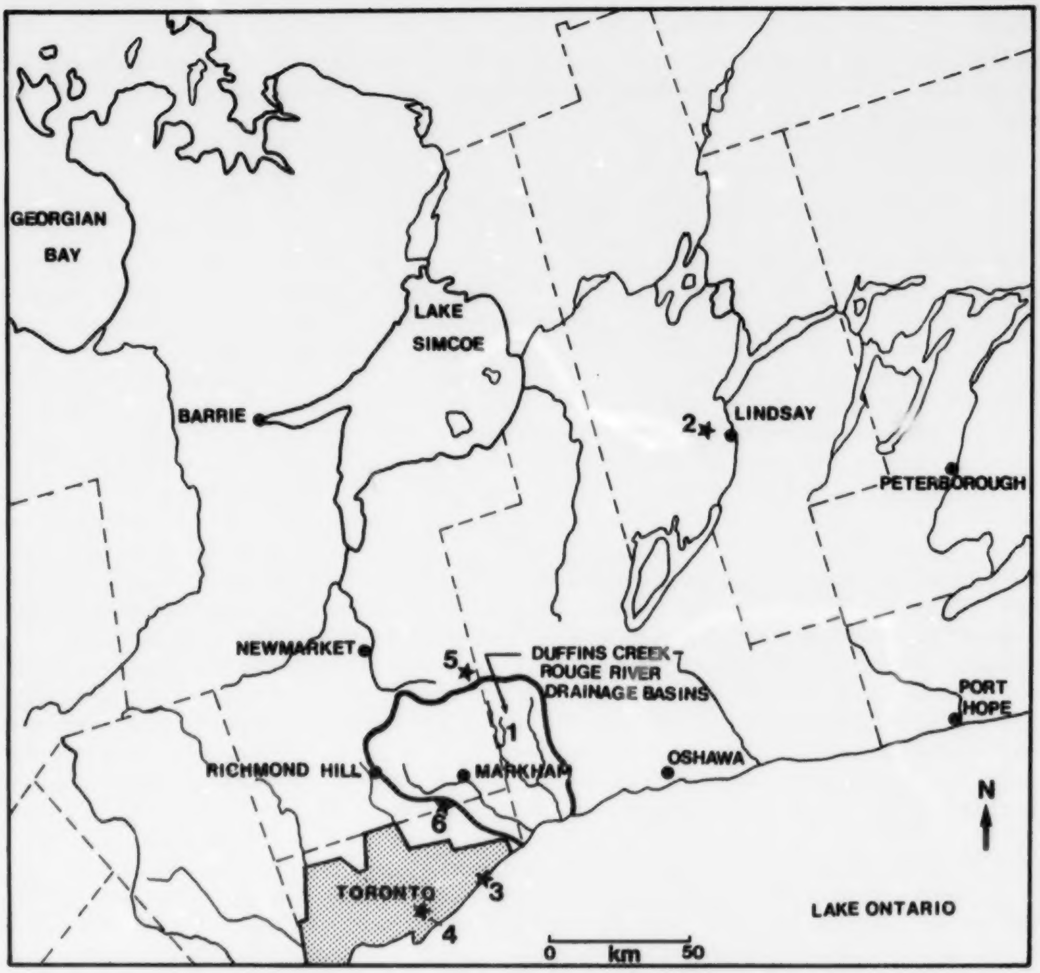

GEORGIAN BAY
LAKE SIMCOE
BARRIE
LINDSAY
2
PETERBOROUGH
NEWMARKET
5
DUFFINS CREEK - ROUGE RIVER DRAINAGE BASINS
1
PORT HOPE
RICHMOND HILL
MARKHAM
OSHAWA
6
N
TORONTO
3
4
LAKE ONTARIO
0 km 50

FIGURE 1 Location of study sites.

NATURAL INORGANIC BACKGROUND GEOCHEMISTRY OF GROUNDWATERS

MAJOR AND MINOR IONS

Groundwaters from shallow surficial sediments of southern Ontario commonly contain total dissolved solids in excess of the 500mg/L maximum desirable level (e.g. Sibul et al.,1977). In such cases a major difficulty lies in determining whether the elevated concentrations reflect contamination of the groundwaters by pollutants or are the result of either natural rock-water interactions or mixing with brackish bedrock waters.

Important preliminary work aimed at identifying natural evolutionary chemical changes in groundwaters as they migrate through local surficial deposits has been conducted in the Duffins Creek - Rouge River Drainage Basins. This study was initiated by Beck (1985) who undertook a comprehensive major and minor ion hydrochemical investigation involving over 260 well water samples (Howard and Beck, subm. C.J.E.S.). Analysed parameters and methods of analysis are summarised in Table 1.

TABLE 1 Chemical parameters and methods of analysis

Parameter	Analytical Technique	Parameter	Analytical Technique
Ca	Atomic Absorption	SO_4	Gravimetric
Mg	Atomic Absorption	HCO_3	Titration
Na	Flame Emission	Cl	Ion electrode/Titration
K	Flame Emission	F	Ion electrode
pH	Ion Electrode	NO_3	Ion electrode
		I	Colorimetry

During the study major ion parameters were plotted on a modified form of Durov diagram (Howard,1985a; Howard,1985b). Shown in Figure 2a, this diagram reveals a number of important features that provide good grounds for separating contaminated from uncontaminated waters. It is significant, for example that the majority of waters occupy a broad elongate field that represents a transition from Ca-HCO_3 to Na(+K)-HCO_3 waters. This type of chemical behaviour is common in many aquifers world-wide and represents a natural chemical evolutionary process in which calcium exchanges with adsorbed sodium as it moves through the system.

Departures from the evolutionary trend indicate an influx of a chemically distinctive water from a different and possibly unnatural source. In the figure, a major departure takes the form of a broad tract in which chloride and nitrate, presumably introduced as contaminants , compete with bicarbonate as the dominant anion. Significantly, calcium remains the dominant cation in most of the contaminated waters.

The Durov representation provides the basis for a more rigorous classification of water types (Howard and Beck, op.cit.). This is shown on Figure 2b. In this classification water Types 1A through 4A represent naturally evolving, uncontaminated waters. Types 1S, 1N and 1U through 4U represent anomalous waters characterized by an unusually high proportion of nitrate and chloride. The designations S and N are applied where the suspected sources of contamination are either road salts or nitrate fertilizers respectively. Where the evidence is less conclusive, contaminated waters are designated with a U (undifferentiated). The distribution of chemical water types in the Duffins Creek - Rouge River drainage basins is shown in Figure 3.

The importance of this work becomes clear when the major and minor ion chemical characteristics of the water types are considered. These are shown in Table 2. Significantly all naturally evolving, uncontaminated, type 1A through type 4A waters display extremely low levels of NO_3 (< 10 mg/L) and Cl (< 5mg/L-1A; < 10 mg/L-2A; < 15 mg/L-3A and 4A), suggesting that concentrations of NO_3 and Cl above levels as low as 15 and 20 mg/L respectively can be

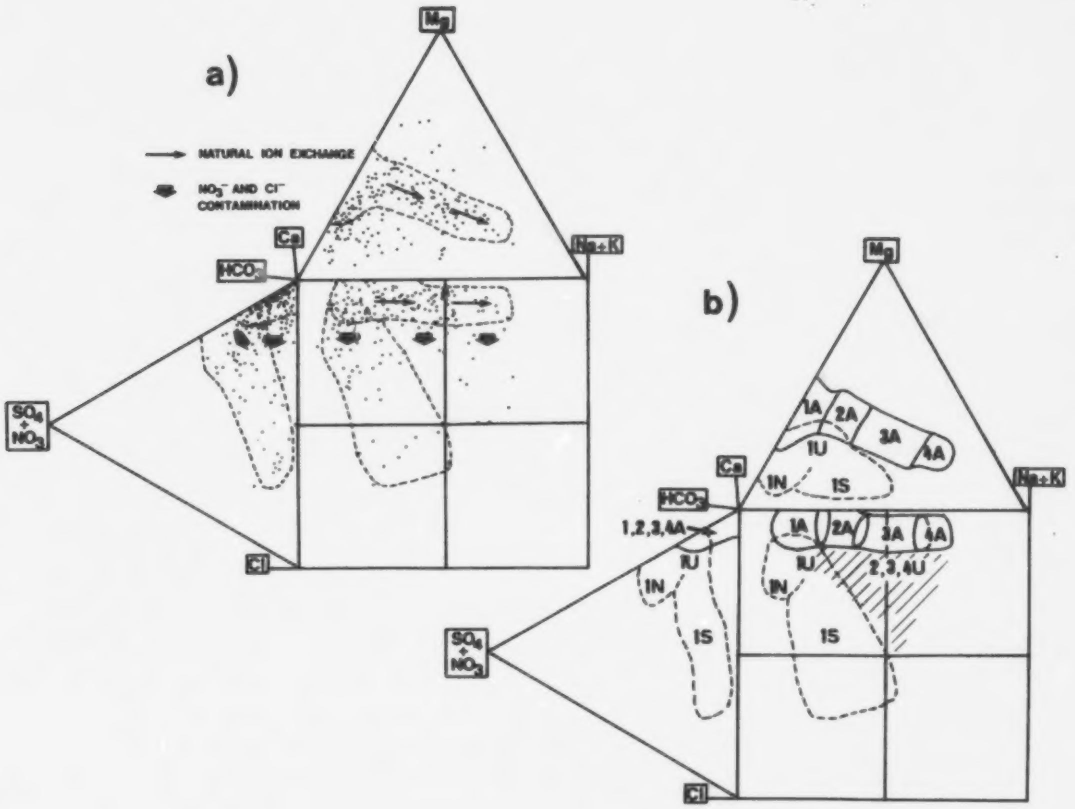

a)
Mg
NATURAL ION EXCHANGE
NO3⁻ AND Cl⁻ CONTAMINATION
Ca
Na+K
HCO3⁻
SO4 + NO3
Cl
b)
Mg
1A
2A
3A
4A
1U
1N
1S
Ca
Na+K
HCO3
1,2,3,4A
2,3,4U
SO4 + NO3
Cl

FIGURE 2 Hydrochemical classification of the groundwater types using a modified form of Durov Diagram.

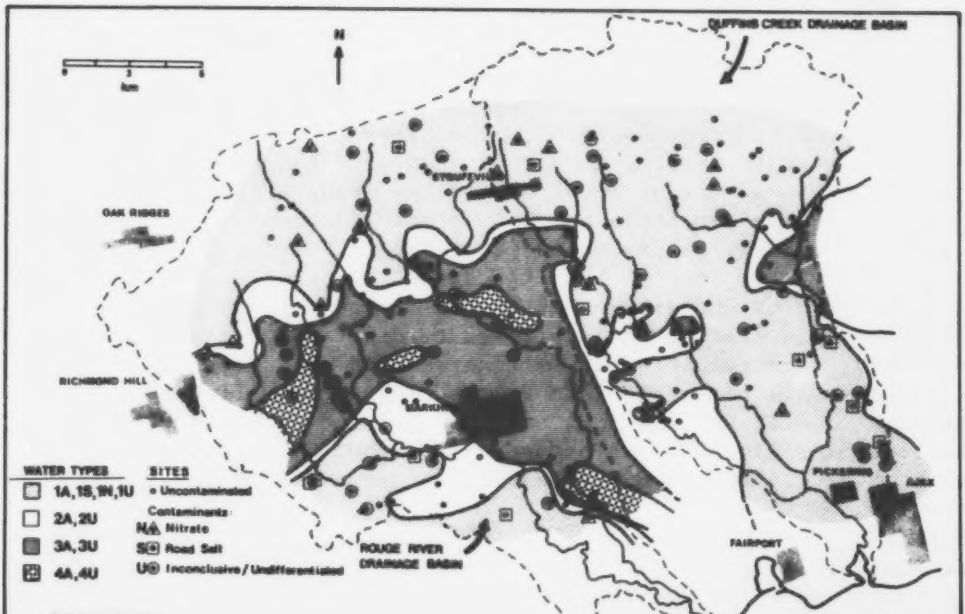

N
km
DUFFINS CREEK DRAINAGE BASIN
OAK RIDGES
STOUFFVILLE
RICHMOND HILL
MARKHAM
PICKERING
AJAX
FAIRPORT
ROUGE RIVER DRAINAGE BASIN
LAKE ONTARIO
WATER TYPES
1A,1S,1N,1U
2A,2U
3A,3U
4A,4U
SITES
Uncontaminated
Contaminants:
N Nitrate
S Road Salt
U Inconclusive/Undifferentiated
Catchment boundary

FIGURE 3 The distribution of chemical water types in the Duffins Creek - Rouge River drainage basins.

an indication of at least minor contamination. It is also significant that iodide levels remain low (<10ug/L) in both contaminated and uncontaminated Type 1 waters.

TABLE 2 Major and minor ion characteristics of the water types

Water Type	Parameter					
	Ca epm^1%	Na epm^1%	Cl mg/L	NO_3 mg/L	Cl/NO_3	I ug/L
Uncontaminated						
1A	>40	<10	<5	<10	-	<5
2A	<60	>10 but <25	<10	<10	-	<10
3A	<50	>25 but <50	<15	<10	-	<20
4A	<35	>50	<15	<10	-	>15
Contaminated						
1S	>40	<25	>40	<10	>25	<10
1N	>40	<50	-	>10	<0.5	<10
1,2,3,4U	-	-	>15 or	>10	-	-

——— diagnostic characteristic
- indicates parameter variable

1 epm = (mg/L x valency)/ formula weight

TRACE ELEMENTS

Having established major ion criteria for identifying naturally evolving, uncontaminated groundwaters the next stage of the investigation involves the determination of the groundwaters' trace element characteristics. Although the eventual aim is to develop an understanding of the "background" trace element geochemistry of the groundwaters as they evolve through water Types 1A, 2A, 3A to 4A, current emphasis has been placed on chemically immature Type 1A waters and their mildly contaminated counterparts - Types 1S, 1N and 1U.

During this part of the study most of the groundwater samples were collected from domestic wells that had been allowed to discharge for some time to minimise potential contamination by well screen and pump fittings. 250 mL trace element samples were collected into Nalgene bottles and filtered under pressure through a 0.45 um cellulose acetate membrane before acidifying with 2.5 mL of Ultrapure nitric acid. A second, untreated 250 mL sample was collected for anion analysis and both samples were transported to the laboratory under refrigeration.

Trace element analysis was carried out using an ARL34000 inductively coupled plasma - atomic emission spectrometer (ICP - AES). Although this machine can lack analytical sensitivity when compared to other methods of analysis it does have the capability for rapid and simultaneous analysis of up to 31 elements in small 5 mL samples, thus minimising the considerable risks of sample contamination. Determined parameters together with theoretical detection limits (T.D.L) and practical limits of determination (5x T.D.L.) are listed in Table 3. To improve the overall sensitivity of the method by ten-fold, samples with volumes greater then 50 mL were pre-concentrated by routine evaporation techniques.

TABLE 3 Parameters determined by ICP -AES analysis (Units mg/L)

Element	Theoretical Detection Limit	5x T.D.L.	Element	Theoretical Detection Limit	5x T.D.L.
Be	0.00029	0.001	Ca	0.0014	0.007
Ba	0.00025	0.001	Zn	0.004	0.02
Fe	0.0012	0.006	Cu	0.0023	0.0115
Cr	0.0024	0.012	Sb	0.0377	0.1885
S	0.0132	0.066	Pb	0.0460	0.23
Mg	0.0137	0.0685	Cd	0.0032	0.016
As	0.0226	0.113	Co	0.0034	0.017
V	0.0016	0.008	Ni	0.0137	0.0685
Se	0.0823	0.2115	P	0.0357	0.1785
Mo	0.0068	0.034	B	0.0045	0.0225
Al	0.0164	0.082	Mn	0.0006	0.0030

To date a total of 76 well water samples have been collected for trace element analysis in the Duffins Creek - Rouge River drainage basins. Although much of these data is still being compiled and processed, preliminary results for representative analyses summarised in Table 4 provide a good indication of the low trace element background in recent, uncontaminated Type 1A groundwaters. In all cases the trace metal concentrations are below recommended water quality guidelines.

INORGANIC GEOCHEMISTRY OF GROUNDWATERS IN AQUIFERS UNDERLYING URBAN AREAS AND ADJACENT TO SALTED HIGHWAYS

URBAN AREAS

Although the Duffins Creek - Rouge River drainage basins provide a good opportunity to investigate the natural geochemical evolution of groundwaters in shallow surficial sediments, an interpretation of the many instances of low level contamination in the basins is complicated by the wide range of agricultural, urban and domestic point and non-point contaminant sources. To overcome these complications it became necessary to extend the study to other localities where the sources of contamination could be more clearly identified.

The impact of urban development on shallow groundwater quality is being studied through comprehensive inorganic geochemical analysis of groundwaters that discharge as contact springs along the Scarborough Bluffs of eastern Metropolitan Toronto (Figures 1 and 4). The Scarborough Bluffs, up to 100m

TABLE 4 ICP - AES analysis of representative Type 1A groundwaters (Units mg/L)

Element	Site #				
	83-110	83-111	83-117	82-34UF	83-19F
Mn	0.0186	0.0142	0.0136	0.0362	0.0421
P	0.0192	0.0202	<0.018	0.097	<0.018
Mo	<0.003	<0.003	<0.003	<0.003	<0.003
Ca	50.43	55.63	54.07	42.77	48.12
Al	0.030	0.048	0.027	0.031	0.074
Zn	0.013	0.044	0.025	0.103	0.088
Ni	0.007	<0.007	<0.007	<0.007	0.011
Fe	1.37	1.03	0.78	0.65	0.10
Mg	16.7	14.6	14.0	24.4	18.9
Pb	<0.02	<0.02	<0.02	<0.02	0.024
Cu	0.007	0.012	0.008	0.007	0.018
Co	<0.002	<0.002	<0.002	<0.002	<0.002
Cr	0.005	0.004	0.006	0.002	0.005
Cd	<0.002	<0.002	<0.002	<0.002	<0.002
S	15.6	21.7	3.3	0.33	3.5
As	<0.01	0.011	0.011	<0.01	<0.01
Se	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	<0.02	<0.02	<0.02	<0.02	<0.02
V	0.002	0.002	0.003	0.003	0.003
B	0.010	0.021	0.015	0.047	0.027
Ba	0.078	0.055	0.053	0.112	0.110
Be	0.0001	0.0002	0.0015	0.0003	0.0001

high occupy about 12km of Lake Ontario shoreline and represent an important discharge zone for a series of minor and largely undeveloped aquifer units defined within a multi-layer sequence of tills, deltaic sands and glaciolacustrine diamicts (Eyles and Eyles, 1983; Eyles et al., 1985). In turn the aquifer units form essentially two composite aquifer systems separated by the Sunnybrook diamict aquiclude. The shallower aquifer system is thought to be only locally extensive and is recharged primarily through areas of the catchment which have recently been transformed from rural pasture to heavily populated commercial and residential areas with some light industry. In contrast the deeper aquifer system appears to form part of a regional flow system which is recharged primarily in rural localities to the north of Metropolitan Toronto.

To the present time a total of 64 samples have been collected from 45 Scarborough Bluffs sites (Figure 4) using sampling procedures that vary according to the nature of the discharge. At sites showing a relatively strong and sustained discharge, the seepage zone is excavated to focus the outflow and samples are collected through a series of bottles connected to a vacuum hand pump. These samples are then divided, the sub-sample for ICP - AES analysis being vacuum filtered and acidified in the field, the sub-sample for anion

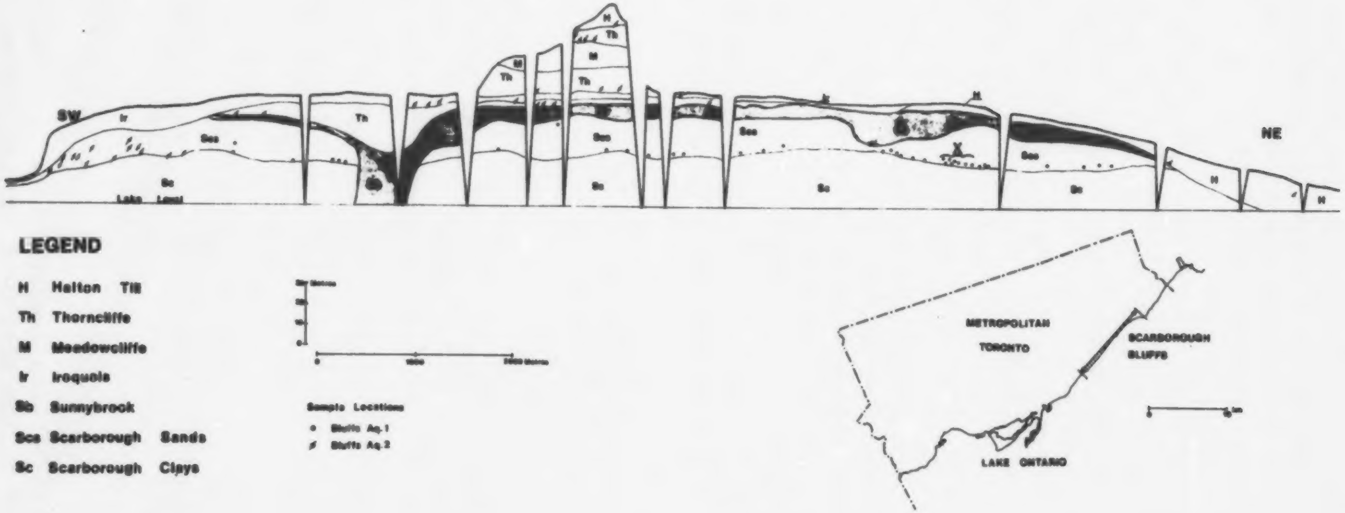

SW
NE
Ir
Sca
Sc
Lake Level
Th
M
H
Sb
LEGEND
H Halton Till
Th Thorncliffe
M Meadowcliffe
Ir Iroquois
Sb Sunnybrook
Sca Scarborough Sands
Sc Scarborough Clays
0
1000
2000 Metres
Sample Locations
Bluffs Aq.1
Bluffs Aq.2
METROPOLITAN
TORONTO
SCARBOROUGH
BLUFFS
LAKE ONTARIO

FIGURE 4 Sampling sites along the Scarborough Bluffs shoreline of Lake Ontario

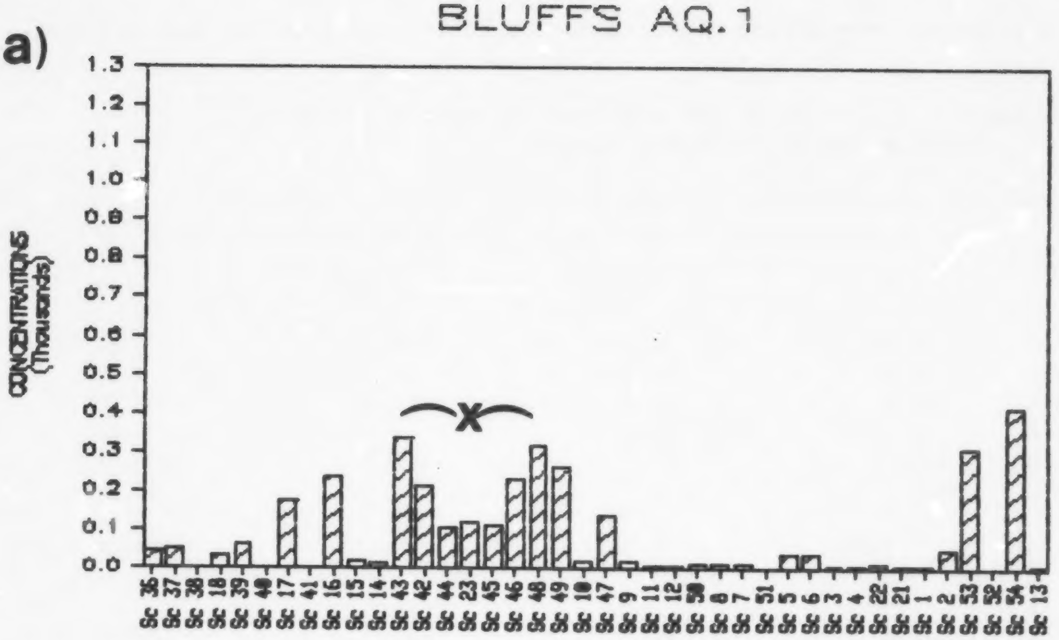
analysis being refrigerated until filtration can be carried out in the laboratory. At sites showing only a weak spring discharge the seepage zone is excavated and samples of saturated material are collected in polythene bags for pore water extraction in the laboratory. Extraction is performed by centrifuging the sediments for 30 minutes at temperatures of 4°C and speeds of 2500 RPM in a Silencer Model H-103FRS floor-mounted centrifuge.

Preliminary major ion analyses of bluff spring waters reveal significant differences in chemical character between groundwaters from the Scarborough Sand aquifer unit underlying the Sunnybrook diamict (Bluffs Aq.1 samples) and groundwaters taken from aquifer units either above the Sunnybrook diamict or from the Scarborough Sand aquifer unit where the Sunnybrook diamict is absent (Bluffs Aq.2 samples)(see Figure 4). Representative major ion analyses of the spring waters are shown in Table 5 and reveal a considerable enrichment in chloride and nitrate concentrations that can presumably be attributed to regional urban development. The effects are particularly well illustrated by the chloride bar graphs shown in Figure 5 in which Bluffs Aq.2 samples (Figure 5b) display considerably elevated chloride concentrations (averaging 500 mg/L) when compared to Bluffs Aq.1 samples which average 150 mg/L. Even the value of 150 mg/L is unrepresentatively high, being elevated by an anomalous suite of samples from site X on Figure 4. This area is noted for its deep rotational bluff failures and the elevated chloride concentrations are thought to reflect the presence of deep fractures that allow chloride enriched groundwaters from the upper aquifer system (Bluffs Aq.2) to penetrate the Sunnybrook diamict aquiclude and enter the Scarborough Sands (Bluffs Aq.1).

TABLE 5 Representative major ion analyses of Scarborough Bluffs spring waters

Sample	Parameter							
	pH	NO_3 mg/L	Cl mg/L	HCO_3 mg/L	Na mg/L	Mg mg/L	Ca mg/L	K mg/L
Bluffs Aq.1								
Sc14	NA	13.3	10.1	NA	7.25	NA	110	NA
Sc15	NA	4.9	15.5	NA	NA	NA	84	NA
Sc40	7.65	5.3	<5	387	25.0	NA	102	3.7
Bluffs Aq.2								
Sc35	7.15	27.6	241.0	360	80.0	NA	103	3.0
Sc30	7.9	130.2	577.2	201	145.0	NA	440	6.0
Sc27	7.5	46.5	1009	262	412	NA	128	3.5

Trace element studies of the bluffs' spring waters have initially been restricted to a reconnaissance survey of the shallower aquifer system (Bluffs Aq.2). In this preliminary survey none of the samples were pre-concentrated before analysis but, as shown by analytical results for four representative samples in Table 6, concentrations of several trace elements show a notable a)



b)

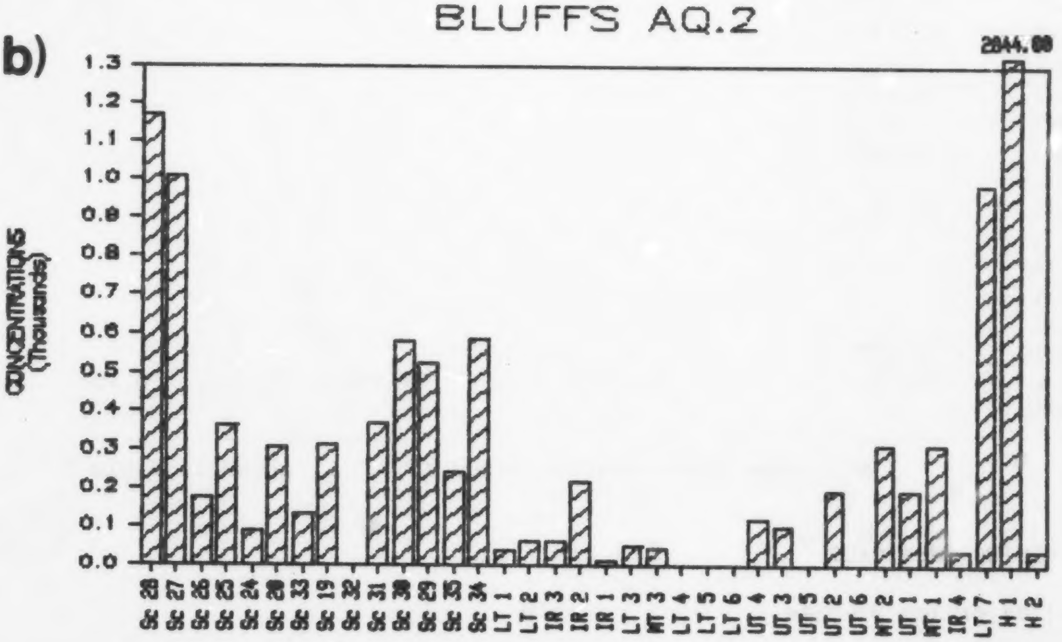


FIGURE 5 Bar graphs showing considerably higher concentrations of chloride in groundwaters from Bluffs Aq.1 as compared to Bluffs Aq.2. (Site X is shown on Figure 4)

presence in waters containing elevated concentrations of chloride and nitrate.

TABLE 6 Representative major ion and trace element analyses of Scarborough Bluff spring samples

Parameter		High chloride/nitrate waters		Low chloride/nitrate waters	
		M1	M4	M5	M6
pH		7.43	7.75	7.11	7.66
NO_3	mg/L	35.44	44.3	8.37	7.74
Cl	mg/L	268.7	315.2	15.43	40.2
F	mg/L	0.57	0.61	0.81	1.62
HCO_3	mg/L	329.4	344.7	317.2	408.7
Na	mg/L	235	300	11.8	43.0
K	mg/L	5.0	3.75	2.0	3.5
Mn	mg/L	0.0204	0.1027	0.158	0.205
P	mg/L	-	-	-	-
Mo	mg/L	-	-	-	-
Ca	mg/L	131.4	145.8	130.3	157.0
Al	mg/L	-	-	-	-
Zn	mg/L	0.0433	-	-	-
Ni	mg/L	-	-	-	-
Fe	mg/L	0.0679	0.028	0.025	0.008
Mg	mg/L	16.17	16.81	25.9	28.7
Pb	mg/L	-	-	-	-
Cu	mg/L	0.0654	0.0123	-	-
Cr	mg/L	-	-	-	-
Co	mg/L	0.0355	-	-	-
Cd	mg/L	-	-	-	-
S	mg/L	22.35	22.89	27.68	43.4
As	mg/L	-	-	-	-
Se	mg/L	-	-	-	-
Sb	mg/L	-	-	-	-
V	mg/L	-	-	-	-
B	mg/L	0.035	-	-	-
Ba	mg/L	0.090	0.302	0.042	0.101
Be	mg/L	-	-	-	-

- indicates concentration below 5x T.D.L. shown in Table 3

ROAD DE-ICING CHEMICALS

Regional Major Ion Studies

Although the Scarborough Bluffs studies clearly demonstrate the influence of urbanization on the quality of shallow groundwaters, the primary sources of the contamination remain speculative until detailed studies on a wide range of urban contaminant sources are completed. In general these sources include disused landfills, leaking waste water systems, urban run-off, and the annual application of nitrogen fertilizers. However, in Metropolitan Toronto, as in many Canadian cities, an additional potential source of contamination takes the form of road de-icing chemicals applied to most major roads and highways. The potentially deleterious effects of road de-icing chemicals on shallow groundwaters have provided the early focus for the current research program.

Preliminary studies were undertaken in Ops township, near Lindsay (Figure 1) (Howard and Falck, in press), where residents had expressed severe disquiet over excessive levels of sodium, chloride and nitrate in groundwaters from their shallow private wells. Whilst the nitrate problem was found to be associated with well drained soils supporting nitrate fertilized agricultural land the elevated chloride concentrations (>40 mg/L) (Figure 6) were found to be closely associated with paved roads which are salted in winter months. In general it was found that wells on the down-flow gradient side of the paved roads were more frequently contaminated than wells on the up-flow side.

The important question concerned whether the contamination resulted from overland flow into and leakage into poorly sealed wells, or was caused by direct recharge and sub-surface transport. This problem was investigated by major cation analyses of the groundwaters and a series of simple laboratory batch experiments designed to determine the degree to which NaCl solutions undergo chemical alteration as they recharge and are transported through the unsaturated zone. Table 7 shows the results of the batch experiments for various types of unconsolidated material. In all cases ion exchange is found to cause a significant depletion of sodium, with the release of calcium accounting for between 40 and 95% of the resulting deficit. This reaction, as previously documented by Howard and Lloyd (1983), takes the form:

$$2Na^{+} + Ca(ad) \rightarrow Ca^{2+} + Na(ad) \qquad (1)$$

TABLE 7 Sodium chloride ion exchange batch experiments

Soil Type	Sample #	Initial Na mg/L	Initial Ca mg/L	Final Na mg/L	Final Ca mg/L	Na adsorbed %	Na adsorbed meq/L	Ca released meq/L
Sand	2	100	0	79	17	21	0.91	0.85
Sand	6	100	0	73	10	27	1.17	0.50
Sand	9	100	0	76	19	24	1.04	0.95
Sand	10	100	0	73	22	27	1.17	1.1
Silt	4	100	0	70	16	30	1.30	0.8
Clay	1	100	0	64	24	36	1.56	1.2
Clay	5	100	0	56	18	44	1.91	0.9
Clay	8	100	0	67	28	33	1.43	1.4

Sodium, calcium and chloride characteristics of groundwaters from the study area are cross-plotted in Figures 7 and 8 and show comparable results. In Figure 7 most of the chloride enriched groundwaters show considerable

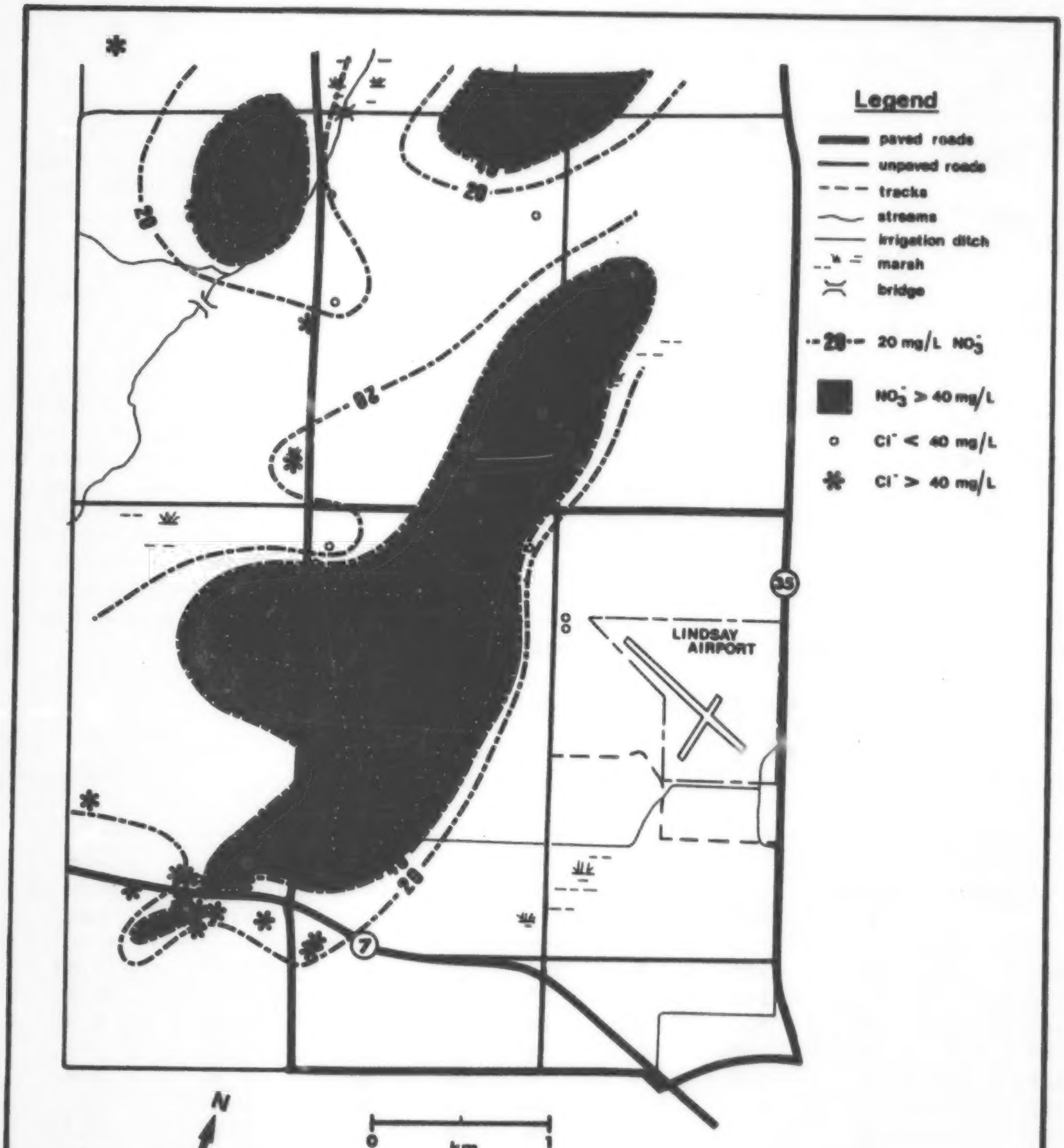

Legend
paved roads
unpaved roads
tracks
streams
irrigation ditch
marsh
bridge
20 mg/L NO3-
NO3- > 40 mg/L
Cl- < 40 mg/L
Cl- > 40 mg/L
20
LINDSAY AIRPORT
35
7
N
0
km
1

FIGURE 6 The distribution of chloride and nitrate contaminated groundwaters in Ops township, near Lindsay.

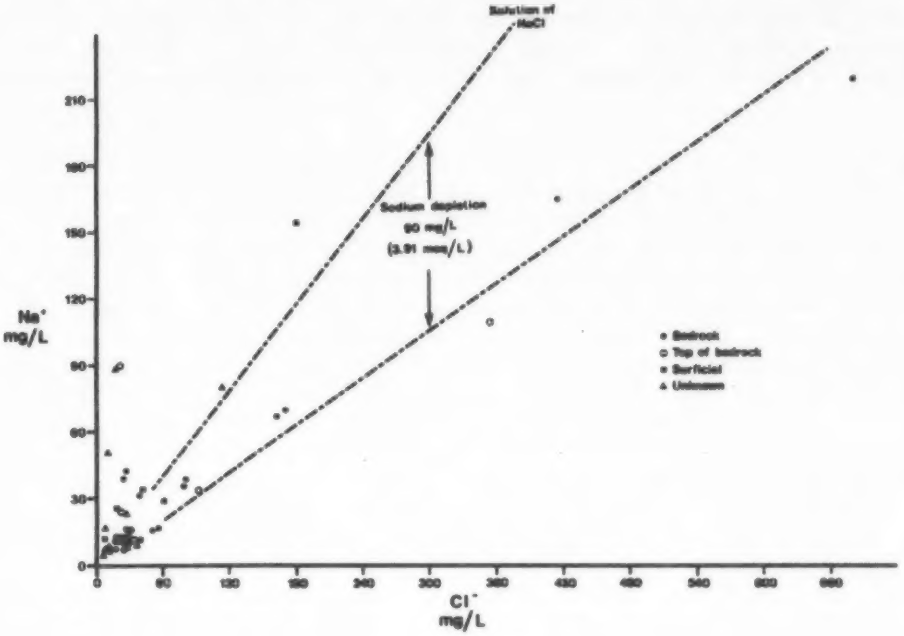


FIGURE 7 Sodium-chloride cross-plot showing sodium depletion in road salt contaminated groundwaters.

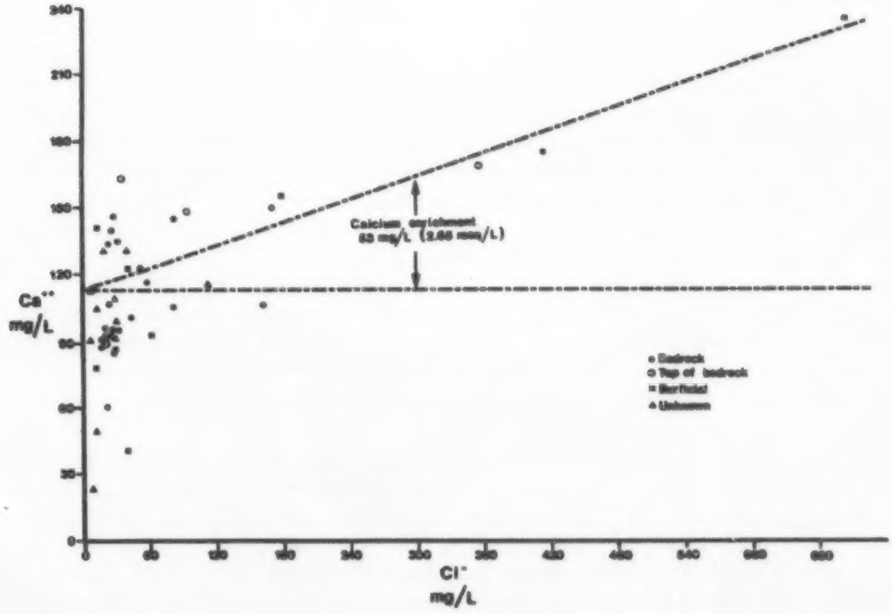


FIGURE 8 Calcium-chloride cross-plot showing calcium enrichment in road salt contaminated waters.

depletion of sodium with respect to the sodium chloride dilution line and according to Figure 8 approximately 70% of the shortfall is compensated through release of calcium. Clearly most of the contaminated wells receive sodium chloride through natural recharge and not as a consequence of poor well design.

In the Duffins Creek - Rouge River drainage basins study area (Figure 2), a considerable number of wells showing elevated chloride concentrations (Type 1S in Table 2) were also found to display greater enrichment in calcium than in sodium. Again road salt contamination was implicated as the source of the chloride contamination with the replacement of sodium by calcium during ion exchange reactions accounting for the anomalously high calcium concentrations. An additional problem in this area, however, concerned a group of chloride enriched waters from relatively deep wells that showed many similarities to road salt contaminated Type 1S groundwaters, particularly with regard to the calcium enrichment. It was suspected that these waters represented an influx of brackish waters from the underlying Ordovician bedrock but major ion data proved inconclusive indicators of source origin. The problem was resolved with minor ion iodide data (Thompson et al., 1985). Figure 9 shows a plot of Log I/Cl against Log Cl for representative waters. I/Cl ratios in rock salt (typically 4.0×10^{-7}) tend to be an order of magnitude lower than the ratio determined for sea water (3.2×10^{-6}). Consequently I/Cl ratios in groundwaters contaminated by road salt tend to be relatively low and, in the event, considerably lower than ratios found in brackish groundwaters from the Ordovician bedrock which show enrichment in iodide with respect to sea water. Clearly the iodide provides a valuable means of distinguishing between two major potential sources of chloride enriched waters.

Site Specific Studies

With the knowledge gained from hydrochemical studies along the Scarborough Bluffs, in Ops township and in the Duffins Creek - Rouge River drainage basins, a series of site specific studies were planned, primarily to to investigate the transport of urban contaminants through the unsaturated zone. For preliminary work 15 drill sites were selected in three areas (Areas 4,5 and 6) on Figure 1. Ten of these sites are in the Don Valley (Figure 10) where Paine (1979) indicated less than 50% of chloride applied as road de-icing chemicals are being removed from the watershed by river flow, implying that the considerable excess (amounting to 25,000 tonnes/annum) is accumulating in the shallow sub-surface. In addition, two sites were selected in the village of Ballantrae Figure 11) where road de-icing chemicals had been implicated in the contamination of domestic wells, and three sites were located in a fallow field area near Milliken to provide some background control.

At each site samples were collected at incremental depths by drilling to the desired depth using a gasoline powered auger, withdrawing the drill rods and extracting a sample of partially saturated sediment using a hand-operated coring device. Samples were transferred to polythene bags sealed with tape, labelled and packed in ice for transport to the laboratory. Pore waters were extracted for chemical analysis using procedures outlined above. The types of analysis conducted depended on the volumes of pore water recovered. Priority was generally given to the major anions; however, major cations, minor ions

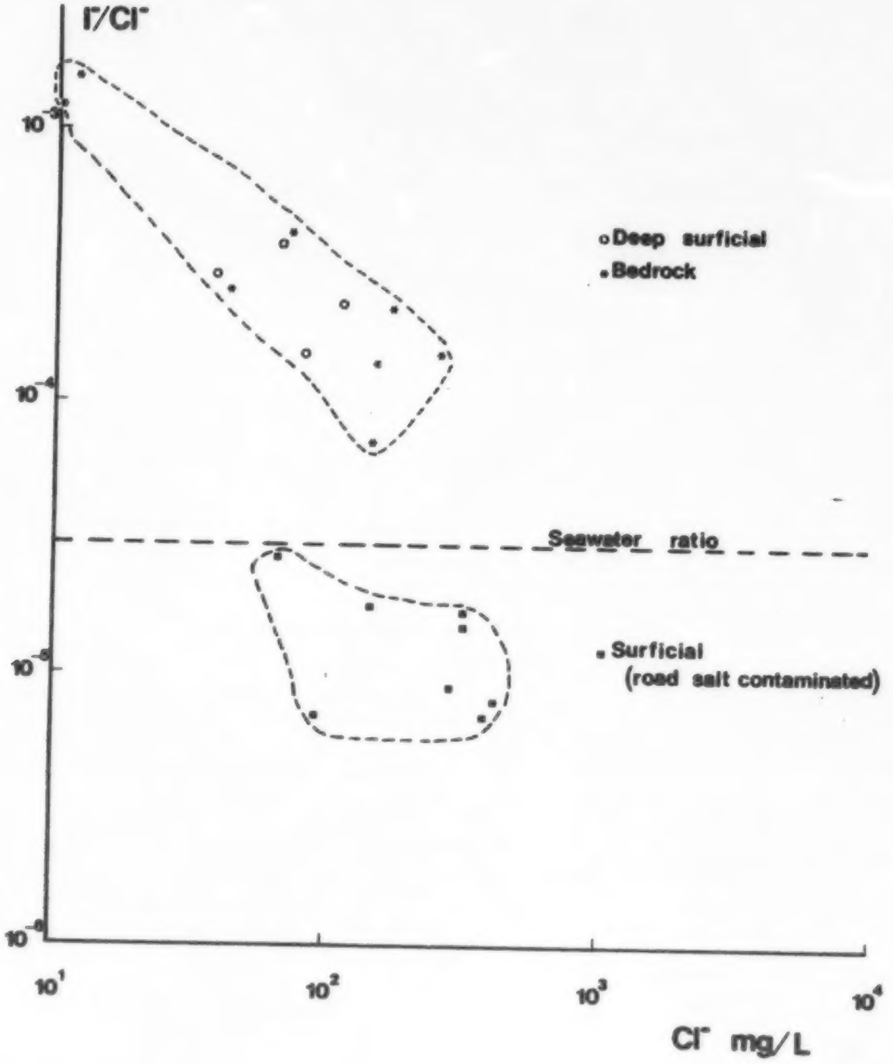


FIGURE 9 Iodide characteristics of chloride enriched groundwaters from the Duffins Creek - Rouge River drainage basins.

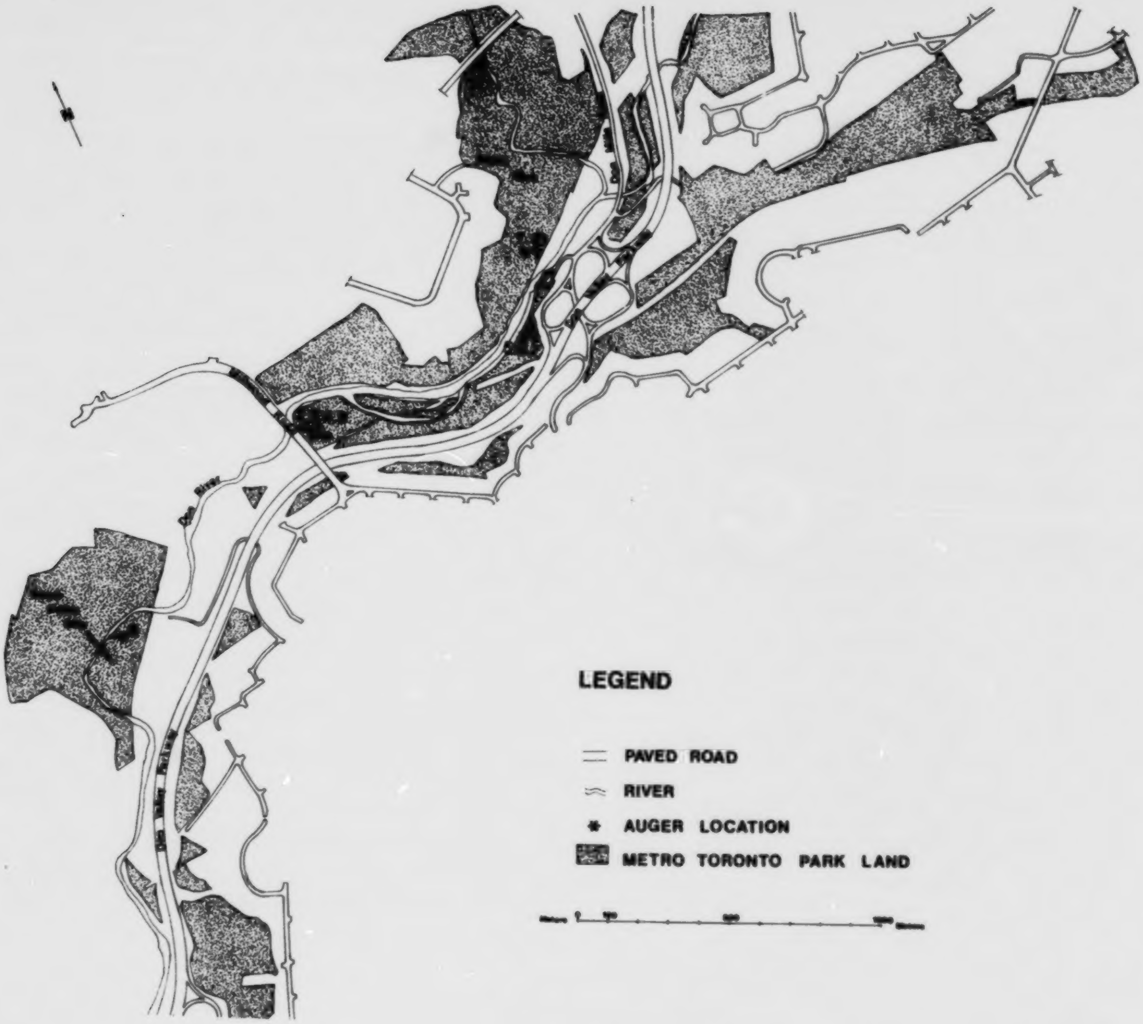

N
Don River
LEGEND
PAVED ROAD
RIVER
AUGER LOCATION
METRO TORONTO PARK LAND

FIGURE 10 Pore water sampling sites in the Don Valley.

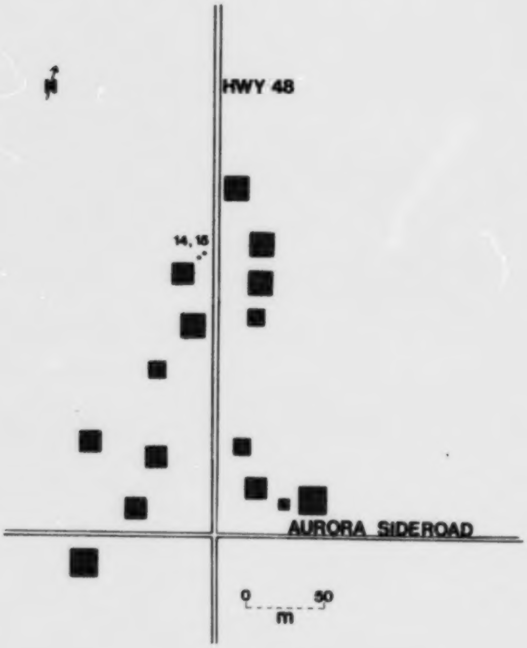

N
HWY 48
14, 15
AURORA SIDEROAD
0
50
m

FIGURE 11 Pore water sampling sites in Ballantrae.

and trace elements were determined where feasible.

Although much of the analytical data is not yet available preliminary results strongly confirm that that the products of urban development are accumulating in the shallow sub-surface environment. Vertical profiles of pore water chloride ion concentrations are shown for the various sites on Figure 12. Sites adjacent to urban roads (sites 2,3,4,5,6,7 and 9 on Figure 10) show highest chloride concentrations ranging from 2000 to 14000 mg/L. The two rural highway sites at Ballantrae (sites 14 and 15) show lower chloride concentrations, ranging up to about 1000 mg/L, but more work is required to explain this difference and to understand the factors controlling the variations with depth exhibited at all the sites.

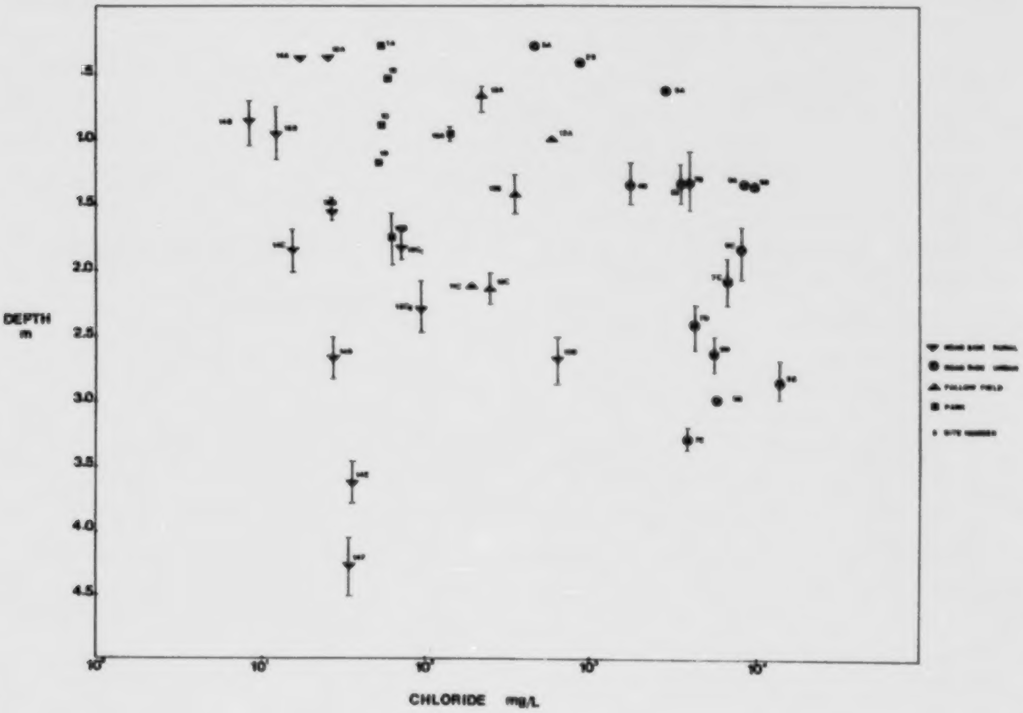


FIGURE 12 Vertical variations in the concentration of chloride in pore waters from the unsaturated zone.

Preliminary results of trace element analyses (Table 8 and Figures 13 and 14) reveal that several of the elements are enriched in pore waters underlying urban road side sites. In the Don Valley concentrations of Cu (0.035 - 0.2 mg/L), Zn (0.02 - 0.2 mg/L), Mn (0.01 - 0.3 mg/L), B (0.03 - 0.25 mg/L) and Ba (0.07 - 0.7 mg/L) are generally significantly above background (Table 4) and this strongly suggests that these elements may support iodide and other minor ions in providing diagnostic signatures of contaminant source origin. In the

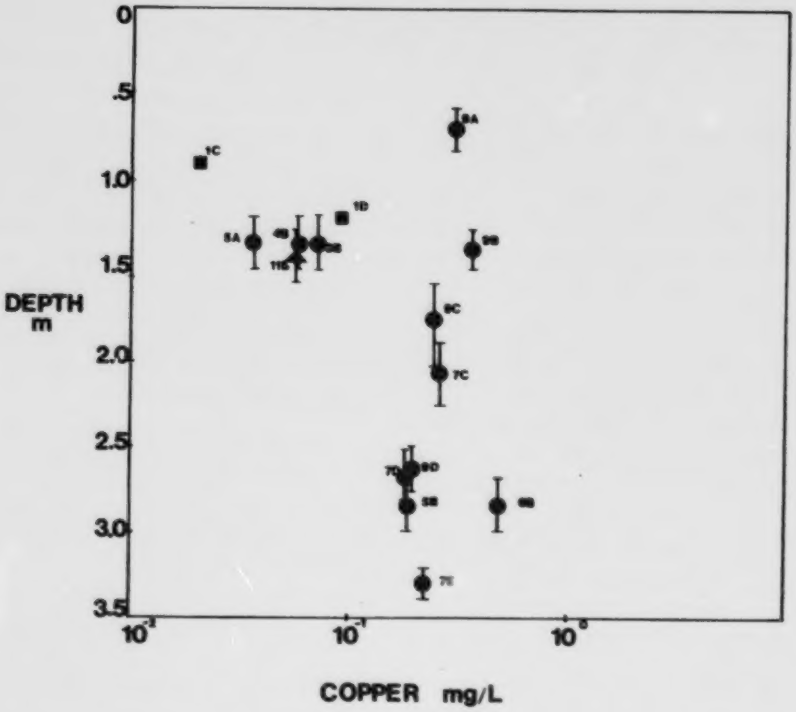


FIGURE 13 Vertical variations in the concentration of copper in pore waters from the unsaturated zone

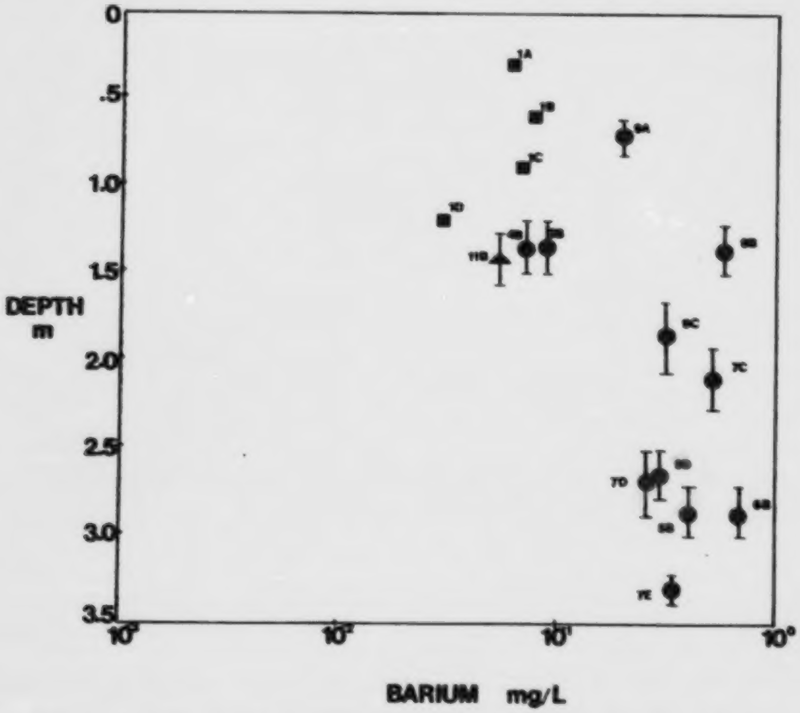


FIGURE 14 Vertical variations in the concentration of barium in pore waters from the unsaturated zone.

latter regard considerable further work has recently been initiated that aims i) to document the major, minor and trace inorganic chemical characteristics of all major urban contaminant sources, and ii) to identify the principle hydrochemical and geochemical controls on the transport of trace inorganic constituents.

TABLE 8 Representative ICP - AES analyses of pore waters obtained from sites in the Don Valley

Parameter		Sample # (for site see Figure 10)			
		9B	7E	6B	5B
Mn	mg/L	0.0376	0.1566	0.2981	0.0784
P	mg/L	0.209	-	-	-
Mo	mg/L	-	-	-	-
Ca	mg/L	551.0	430.0	1066.0	450.0
Al	mg/L	-	0.082	0.140	-
Zn	mg/L	0.051	0.027	0.045	0.022
Ni	mg/L	-	-	-	-
Fe	mg/L	0.038	0.038	0.037	0.027
Mg	mg/L	14.1	17.5	34.4	16.45
Pb	mg/L	-	-	-	-
Cu	mg/L	0.3685	0.2245	0.3877	0.1869
Cr	mg/L	-	-	-	-
Co	mg/L	-	-	-	-
Cd	mg/l	-	-	-	-
S	mg/L	108.6	114.8	171.9	93.77
As	mg/L	-	-	-	-
Se	mg/l	-	-	-	-
Sb	mg/L	-	-	-	-
V	mg/L	-	-	0.011	-
B	mg/L	0.0855	0.1525	0.0357	0.0386
Ba	mg/L	0.5784	0.3353	0.6704	0.3953
Be	mg/L	-	-	-	-

- indicates concentration below 5x T.D.L. shown in Table 3

CONCLUDING DISCUSSION

Despite the relative infancy of the project considerable progress has been achieved in a number of directions. In particular the studies have:

i) developed major ion criteria for recognising low level contamination of shallow groundwaters in surficial sediments;
ii) established background concentrations of a range of minor ions and trace elements in naturally evolving groundwaters;

iii) confirmed that chemical derivatives of de-icing salts applied to urban roads and highways are causing significant contamination of pore waters in the unsaturated zone;
iv) demonstrated the detrimental influence of urbanization on shallow groundwater quality;
v) demonstrated the value of iodide as a means of distinguishing between brackish bedrock waters and road salts as sources of anomalous chloride enrichment in groundwaters from surficial sediments.

Future studies will focus on the regional extent of the urban contamination problem and will examine more closely the nature and behaviour of those trace element constituents showing greatest potential for characterising and identifying contaminant source origins. These studies will involve an escalation of the drilling and sampling programme, comprehensive inorganic chemical analysis of a wide range of potential contaminant sources, geochemical analysis of local host sediments, controlled laboratory experiments to investigate trace element transport and studies of trace metal speciation based on theoretical concepts and chemical computer models.

ACKNOWLEDGMENTS

The authors gratefully acknowledge numerous University of Toronto students and colleagues who provided technical and research assistance. Notable contributions were made by Paul Beck and Bryan Kaye who carried out early "pioneering" studies, Ilze Buivids, Joanne Thompson and Lucy Nolas who undertook many of the major and minor ion analyses and assisted with the drafting, and to Mark Hughes and Philip Haggerty, who in addition to their involvement in sample collection and analysis helped considerably with micro computer data processing. ICP-AES analyses were conducted by N.A. Belicki at the University of Toronto's Institute for Environmental studies. Funding for the study is being provided by grants through NSERC and the Ontario Ministry of the Environment.

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THE EFFECTS OF TILE DRAINAGE AND OPEN DITCHES ON PEAK FLOWS AND DRY WEATHER FLOWS

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Department of Civil Engineering, Queen's University

Key words: Agricultural Drainage, Tile Drainage, Hydrologic Simulation.

ABSTRACT

The project is scheduled for a three-year period and has been designed to assess the effects of tile drainage and open ditches on peak flows and dry weather flows with particular application to Ontario. This study involves (I) the development, calibration and testing of a continuous, physically-based, hydrologic simulation model for tile-drained agricultural fields and basins; (II) instrumentation of tile-drained fields in the South Nation River Basin; and (III) statistical analysis of (a) historical data from ditch and tile-drained fields and basins in the South Nation River basin and elsewhere, and (b) simulated discharges generated by the model developed in (I) above, both on a peak flow and a dry weather flow basis.

The project is presently 8 months into year 1 of its three-year schedule. A worldwide literature survey has resulted in the production of an annotated bibliography for the hydrology of agricultural drainage. Over 400 abstracts covering the period 1970-84 have been collected, catalogued and entered in a database using dBASE III. It is available both in hard copy and on IBM-PC compatible disks.

A physically-based hydrologic simulation model for tile-drained agricultural fields has been developed for the simulation of tile drain discharge under single rainfall events. The model is now being tested and calibrated. Instrumentation has been installed in a tile-drained field to collect rainfall and discharge data over the fall of 1985 for analysis during year 2 of the project.

IMPACTS OF DRAINAGE ON FLOWS

W. E. Watt[1] and J. D. Paine[2]

Abstract

Canada has experienced and will continue to experience unprecedented demands for increased food production and increased agricultural productivity. Because less than 5 percent of the total land in Canada is suitable for cultivation, the reclamation of cultivable land by drainage improvement will continue to accelerate. The effects of this drainage on those rivers and streams that receive waters from drained areas are not clearly understood, but they can be adverse (e.g. increased downstream flooding, reduction in low flows and impaired water quality). A conceptual representation of the drainage process is presented to illustrate the possible impacts of drainage. To obtain evidence of these impacts requires a better understanding of the hydrologic processes involved, systematic data collection at the field level and development of a physically-based, conceptual model for drained fields.

Introduction

The need to increase agricultural productivity through land drainage is obvious to all those in the agricultural sector. At the same time, however, the necessary drainage projects may lead to adverse environmental effects. In particular, they may result in increased peak flows and reduced low flows. The increased peak flows cause erosion and flooding and downstream land owners often demand expensive flood control structures to restore pre-drainage flood levels. The reduced low flows result in impaired water quality conditions and downstream users may demand expensive water storage structures to increase low flows to pre-drainage conditions. Concern over both these effects has led to pressure to delay, defer and cancel drainage projects. However, there is not general agreement on the hydrologic impacts of tile drainage and often claims by both proponents of, and objectors to, drainage projects are speculative.

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Because of this lack of understanding of the overall hydrologic response to agricultural drainage, there is an urgent need for research to evaluate the impacts of drainage and for the dissemination of knowledge as it becomes available to assist in the planning of drainage projects which are technically, environmentally, and economically sound.

Research should be directed towards both statistical analyses and the development, calibration and testing of an agricultural drainage simulation model capable of forecasting the hydrologic impacts of drainage both at the field level and the basin level.

The Physical System

According to Irwin (1977)

> "Agricultural land drainage is the art and practice of reducing the resistance to the outflow of water supplied to land. Its aim is to reduce the water storage in and on the land, both in depth and frequency so that agricultural productivity will be enhanced."

The intent of field drainage is to modify the natural soil-water regime at the field level; however, to achieve this, modifications to a drainage basin beyond the field level are necessary. Tile drains or field ditches must drain to larger channels (municipal drains) with larger cross sections and slopes than natural channels to temporarily store the increased volume of water and remove it quickly to keep the frequency and duration of saturated field conditions to a minimum.

If a representation of the physical system is considered (Fig. 1), the effect of drainage becomes apparent. The natural hydrologic process can be represented by input and output elements connected by storage and routing elements. Agricultural drainage operates on these storage and routing elements.

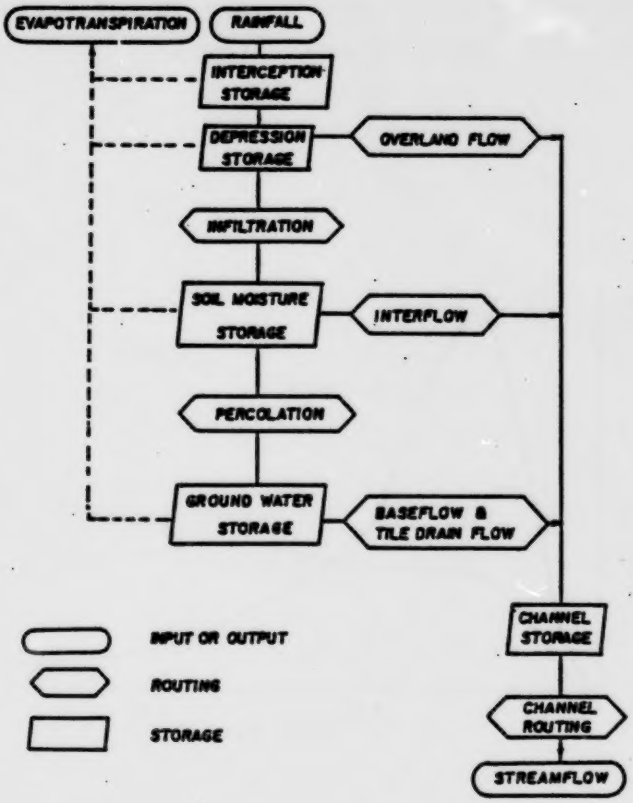
EVAPOTRANSPIRATION
RAINFALL
INTERCEPTION STORAGE
DEPRESSION STORAGE
OVERLAND FLOW
INFILTRATION
SOIL MOISTURE STORAGE
INTERFLOW
PERCOLATION
GROUND WATER STORAGE
BASEFLOW & TILE DRAIN FLOW
CHANNEL STORAGE
CHANNEL ROUTING
STREAMFLOW
INPUT OR OUTPUT
ROUTING
STORAGE

Fig. 1 Representation of a hydrologic system

In general, it is desirable to make the storage components smaller (the exception is channel storage which is usually increased as channel cross sections are enlarged) and to make the routing or transmission elements behave more rapidly. This is achieved by increasing the slopes of drainage ditches, decreasing the roughness through the removal of natural obstructions, shortening flow paths and enhancing soil porosity. The result is that a larger volume of water will be removed from the land in a shorter period of time.

A hydrograph for a drained area (Fig. 2) will exhibit higher peak flows and a faster recession than the undrained case. Higher velocities and discharges could lead to increased erosion and frequency of flooding in drainage channels and receiving water courses.

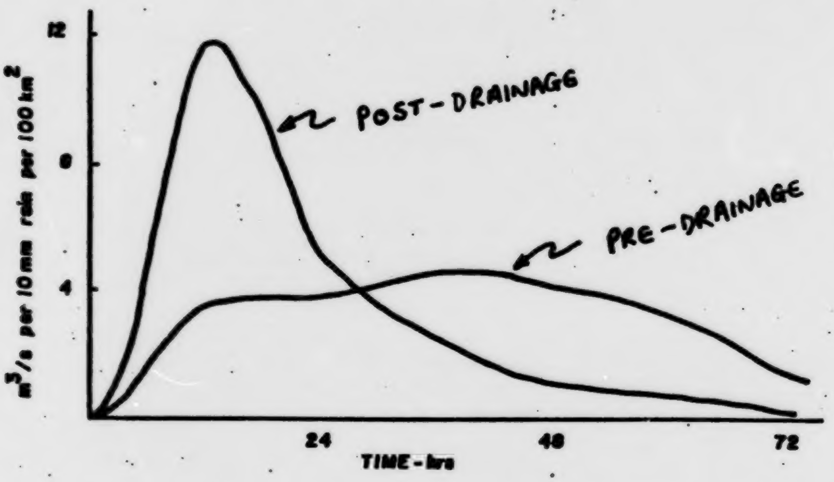

Fig. 2 Pre-and post-drainage hydrographs for the
Nenagh catchment (Ireland)
(after Bailey 1981)

The effects of drainage can also be viewed in a probabilistic sense (Fig. 3). The physical system represented in Fig. 1 operates on the input (the rainfall/snowmelt time series) and converts it and its associated frequencies to an output (flows and volumes). Drainage alters the operator and hence alters the frequency characteristics of the output. Although the frequency of crop innundation or root zone saturation in the field will be reduced, the frequencies of peak flows and volumes downstream are likely to increase.

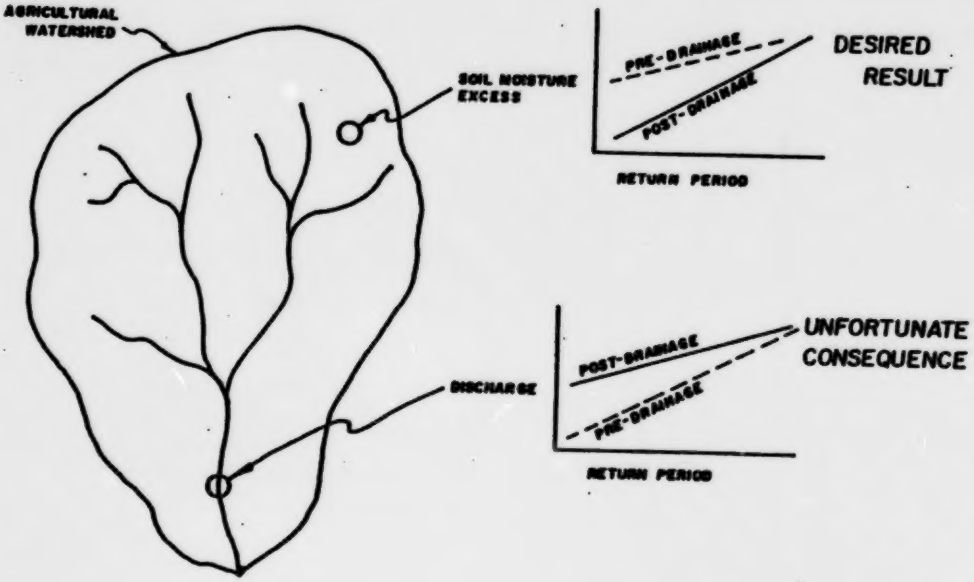
AGRICULTURAL WATERSHED
SOIL MOISTURE EXCESS
PRE-DRAINAGE
POST-DRAINAGE
DESIRED RESULT
RETURN PERIOD
DISCHARGE
POST-DRAINAGE
PRE-DRAINAGE
UNFORTUNATE CONSEQUENCE
RETURN PERIOD

Fig. 3 Impact of drainage on downstream peak flows

Evidence of the Effects of Drainage of Flows

Unfortunately where data exists to support the premise of increased downstream flows, it is usually site specific and often sketchy. However, some knowledge can be gained by analogy. The actions of removing water storage elements and increasing the efficiency of transmission elements do indeed increase peak flows and volumes for a specific event or increase frequencies of higher flows for a series of events for two cases that are well documented; these are urbanization (Fig. 4) and deforestation. Similar effects will result from reduced storage and faster transmission through the implementation of drainage projects.

The actions of urbanization and deforestation on a watershed are more drastic 'shocks' than agricultural drainage. If the impact of an operation is proportional to its magnitude, urbanization and deforestation could be considered as first order shocks. Agricultural drainage is then a second-order shock and consequently, its impacts will be more difficult to observe.

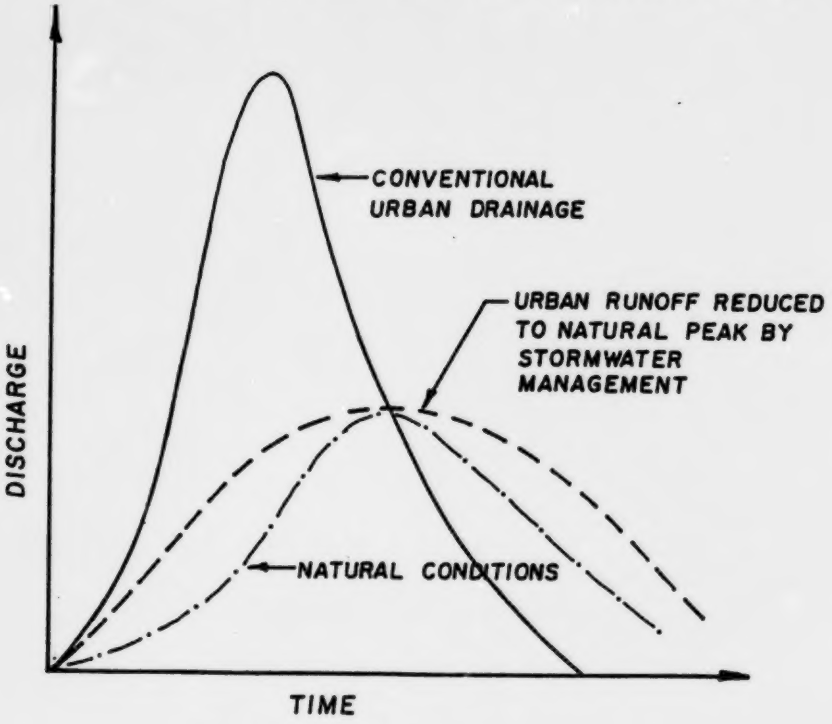

Fig. 4 Urban runoff

Recently, the National Hydrology Research Institute completed a review of the effects of agricultural land drainage on streamflows through a literature survey (NHRI 1982). Their findings, in conjunction with research performed in the United States and Ireland, lead to the following.

(1) Land drainage does have a significant impact on stream hydrographs. The effects of channel improvements overshadows effects due to draining depressions or modifying the soil-water regime by tile drainage.

(2) The magnitude and timing of impacts are variable; they depend on the work done, its location in the watershed, and the physical characteristics of the basin.

(3) Existing hydrologic theory is inadequate. Existing models are often oversimplified and possess incorrect or inadequate submodels.

(4) Knowledge at the field level and of processes in the unsaturated zone is lacking.

To obtain evidence of the impacts of drainage on flows, there are two general approaches. The first is to examine flow records for trend. The second method is to develop a hydrologic model which is capable of accurately simulating the response of the system and then to operate the model with typical meteorological inputs and with model parameters corresponding to drained and undrained conditions.

Trend Analysis to Obtain Evidence of Drainage Impacts

As indicated above, one method to obtain evidence of drainage impacts is to examine flow records for evidence of non-stationarity that is statistically significant. This non-stationarity could be in the form of either a jump or a trend which may be evident in one or more statistics of the flow series (e.g. mean, maximum, minimum) or to the frequency distribution of one or more of these statistics. For reliable trend analysis, a long period of flow record (> 25 years) for a basin in an undrained state followed by an equally long period of record for the same basin in an extensively drained state would be ideal. Over the total period, all other factors (average precipitation, temperature, etc.) should be constant. Generally, a much shorter period of record exists with a large number of factors changing and with the drainage process itself extended through the period of record. The following factors must be taken into account when examining the record statistically and looking for trend:

i) the influence of climatic changes,

ii) the rate of drainage activity,

iii) the location of the drainage and its time of implementation within the watershed,

iv) the type of drainage (tile vs. outlet drain construction),

v) the influence of changes in crops grown and agricultural practices (often a direct result of drainage), and

vi) physical changes in the watershed with time that have nothing to do with drainage (sedimentation, urbanization, river crossings, etc.).

Because of the random nature of flows, a lengthy period of record, often with very extensive drainage works, is required to obtain statistically significant and identifiable trends. Even if a trend can be identified, the unfortunate fact remains that the results are site specific. Appreciation of the result of drainage without an understanding of the intricate subprocesses limits the ability to transfer the results to other locations.

Recent research in the United Kingdom (Bailey 1981) appears to illustrate a relatively successfully application of trend analysis. Twelve catchments in Ireland were examined, each with an average of 10 years of record prior to and after drainage. Flood peaks were examined and analysed for pre- and post-drainage conditions (Fig. 5). The responses of the catchments were substantially altered by tile and mole drainage in fields, ditching and improvement of main arterial channels and river controls.

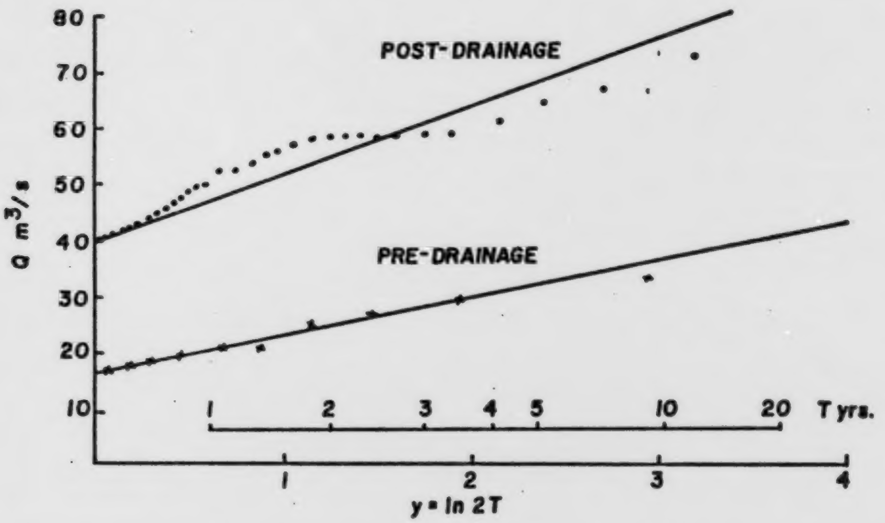

Fig. 5 Pre- and post-Drainage frequency relations for the Nenagh catchment (Ireland) 318 sq.km.

Fig. 6 illustrates the results of a split record test performed to assess the possibility that the frequency shift may have been due to climatic changes over the period of record, i.e. increased post drainage flows might be due to wetter, more flood producing weather having occurred in the post-drainage period than the pre-drainage period. The record on the Brosna, which was unaltered over the periods in question, was divided into the same pre and post-drainage periods as recorded on the Killimor River. Because the frequency curve for the Brosna is virtually identical for both periods of record, the frequency shift on the Killimor cannot be attributed to a change in climate.

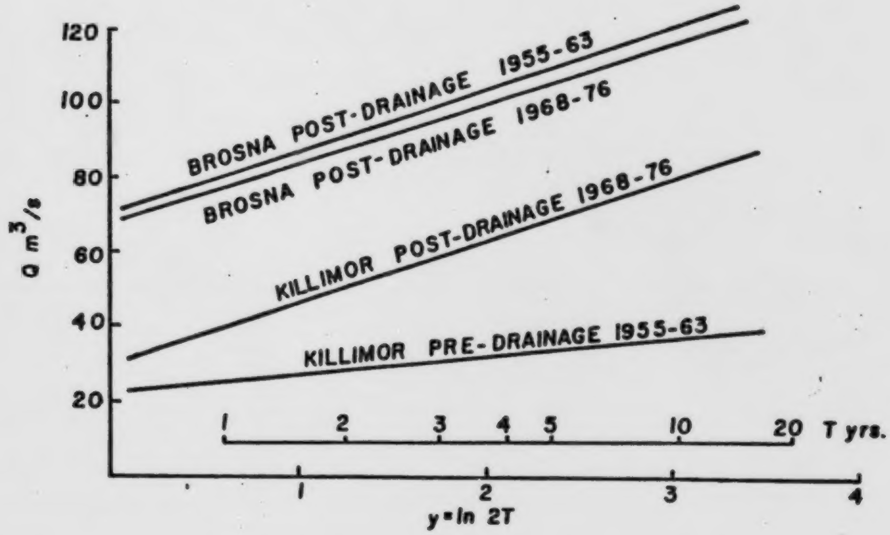

Fig. 6 Split record test of the river Killimor 206 sq.km.

Modelling the System to Determine Drainage Impacts

Using a model to assess the effects of drainage involves developing a mathematical model to represent the basin in question, ideally, the model should have submodels for each storage and routing function. Following calibration and verification of the model using observed data, the model parameters are changed to simulate drainage conditions. The model is then applied in both the 'natural' and 'drained' states for the same input time series and the results compared.

Requirements to ensure that models will allow an accurate assessment of the impacts of drainage are listed below.

(1) A first priority is long term monitoring both for a drained basin and a physiographically/climatologically similar undrained basin. Measurements must include discharge and water table heights at various points as well as meteorological data (temperature, precipitation).

(2) Soil-water models which adequately simulate surface and subsurface drainage at the field level over an entire year should be developed and calibrated.

(3) The combination of (2) with standard routing routines to create a basin-wide model capable of simulating various types of drainage works in various locations will permit the evaluation of the effects of these works.

Present Research - Model Development and Field Work

Research is directed towards the development of a conceptual model to represent the drainage process at the field level. Simultaneously, data are being collected to allow model calibration and to gain a better understanding of physical processes. The event model is designed to simulate surface runoff, tile flow, soil moisture and water levels from a tile-drained field. An event, which consists of rainfall and the subsequent runoff, may last from 1 hour to 2 weeks.

Fig. 7 illustrates the various processes involved in the real system which must be accounted for in the model. Fig. 8 shows the representation of the real system by the model.

Field Location and Data Collection

A 14 ha tile-drained field in the South Nation Basin has been instrumented. A collection box with a V-notch weir and charting water level recorder are installed at the outlet of the main collector drain. Piezometer tubes located in the field are read manually once per week at the time of chart changes. A tipping-bucket rain gauge also with an 8 day chart is located approximately 1 km from the outlet. This instrumentation was installed in June, 1985 and the intent is to leave it in place for at least a 2-year period.

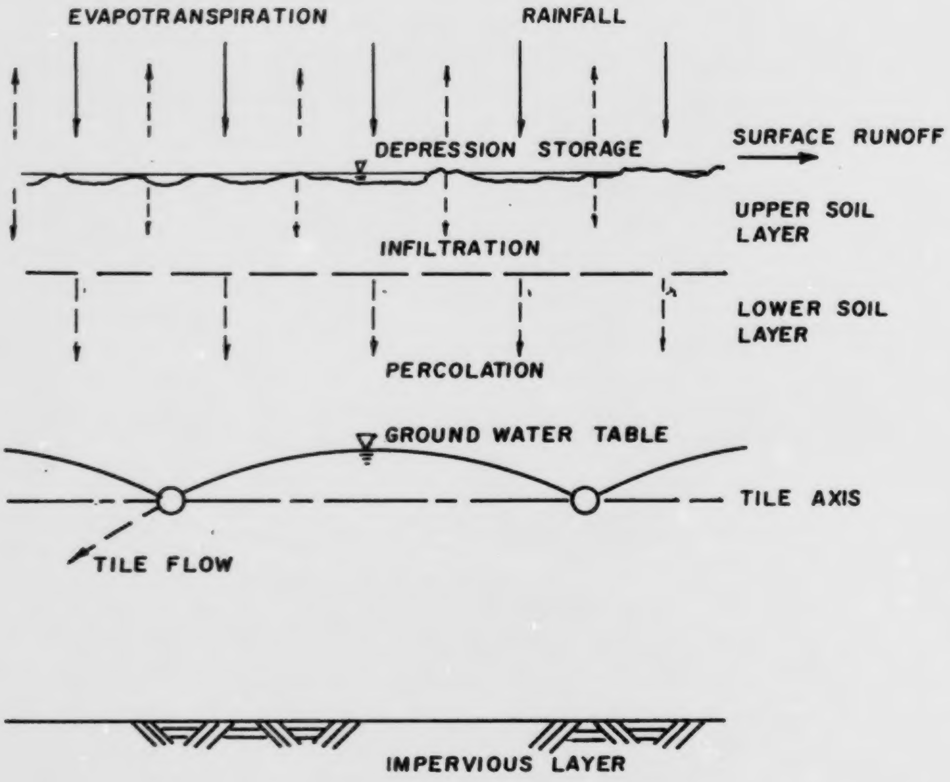
EVAPOTRANSPIRATION
RAINFALL
DEPRESSION STORAGE
SURFACE RUNOFF
UPPER SOIL LAYER
INFILTRATION
LOWER SOIL LAYER
PERCOLATION
GROUND WATER TABLE
TILE AXIS
TILE FLOW
IMPERVIOUS LAYER

Fig. 7 Schematic of the drainage system at the field level

Additional work is ongoing to locate a suitable field in the Kingston area, with the assistance of the Ontario Ministry of Agriculture and Food. This will allow an additional data base and will be somewhat more convenient because of its proximity to Queen's University.

Next Step

The next step in the work is to extend the field model to a basin wide model to ascertain the distributed effects of agricultural drainage on flows to receiving water bodies.

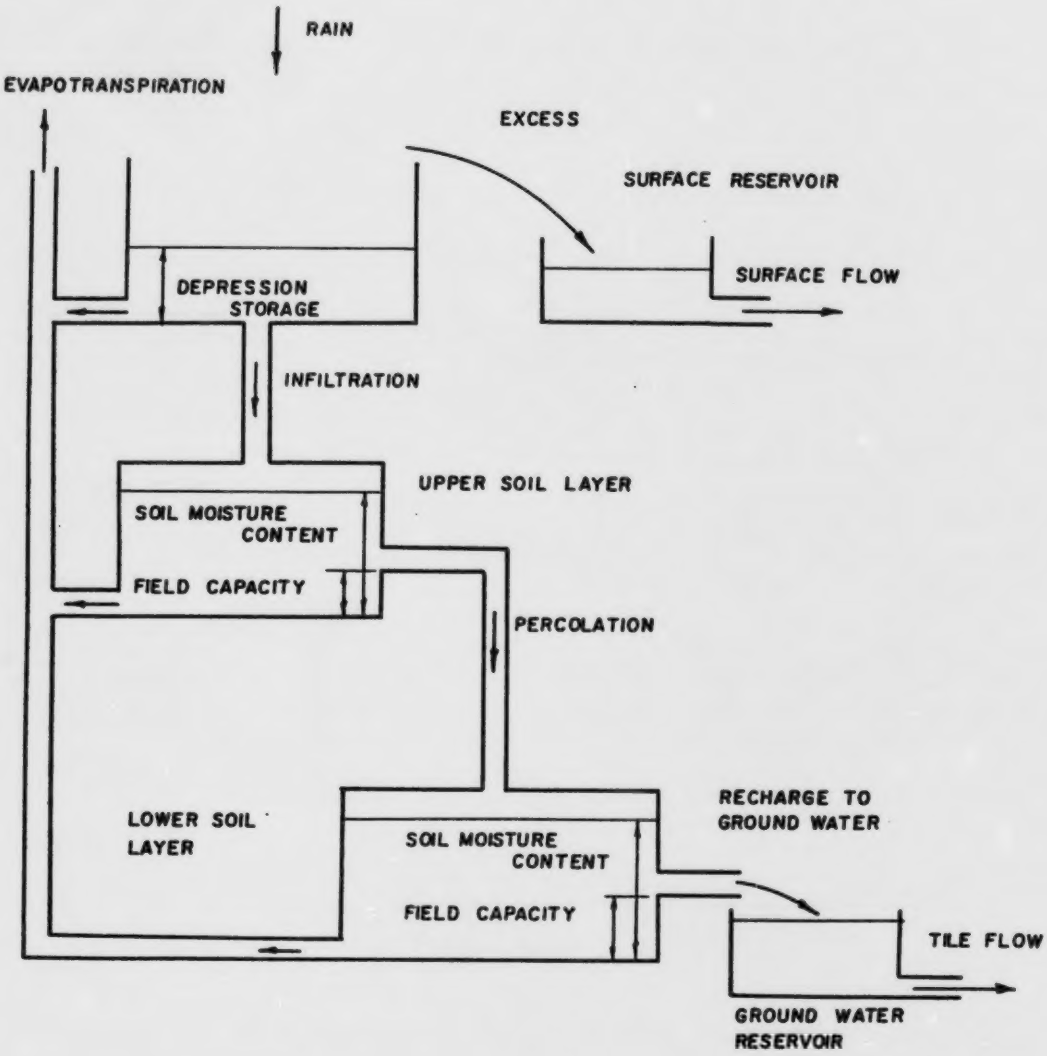
RAIN
EVAPOTRANSPIRATION
EXCESS
SURFACE RESERVOIR
SURFACE FLOW
DEPRESSION STORAGE
INFILTRATION
UPPER SOIL LAYER
SOIL MOISTURE CONTENT
FIELD CAPACITY
PERCOLATION
LOWER SOIL LAYER
RECHARGE TO GROUND WATER
SOIL MOISTURE CONTENT
FIELD CAPACITY
TILE FLOW
GROUND WATER RESERVOIR

Fig. 8 Model Representation of the tile-drained field

Finally, once the processes are understood and can be modelled, the knowledge should be disseminated so the models can be used as a design tool by practicing engineers, agricultural scientists, economists and planners.

Acknowledgements

This paper is a result of ongoing work in the Department of Civil Engineering at Queen's University for the Ontario Ministry of the Environment (Project #152 PL).

References

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2. Irwin, R.W., 1977. Economics of Farm Drainage in Ontario, Paper presented to the CWRA Conference on Agricultural Land Drainage held at Cambridge, Ontario.

3. N.H.R.I., 1982. Agricultural Land Drainage, National Hydraulic Research Institute, Research Project, Ottawa, Canada.

PRE-FEASIBILITY STUDY ON EXPANSION AND UPGRADING OF PORT DOVER SEWAGE TREATMENT PLANT

Maria Kelleher, Maclaren Engineers Inc.
Cris Papadopol, Ontario Tree Improvement and Forest Biomass Institute,
Ministry of Natural Resources

Key words: Port Dover, Sewage Treatment, Activated Sludge, Biological Contactors, Aeration Devices, Tree Farm, Lagoons, Effluent.

ABSTRACT

The existing Port Dover Water Pollution Control Plant is a primary plant with phosphorus removal and has been subject to a number of operating problems during the last few years. A study was commissioned to review these problems and evaluate a number of options for expanding and upgrading the plant to provide secondary treatment.

The following options were considered:

- Conventional Activated Sludge
- Rotating Biological Contactors
- Biological Aerated Filters
- Extended Aeration, and
- Tree Farm

Two of the options considered are innovative concepts which have not been used in plants in Canada to date. The first is the biological aerated filter, marketed by Envirotech. It consists of a steel tank filled with fired clay media. Effluent is introduced at the top of the media, the upper section of which accomplishes biological treatment, and the lower section of which acts as a clarifier. The major advantage of this system is the low space requirement, and the fact that no secondary clarifiers are required, thus saving considerable capital cost.

The tree farm design involves storing sewage in a lagoon system and spray irrigating a tree farm with the effluent. In this manner, nutrients in the effluent enhance growth of the trees, and evapotranspiration from the leaf surfaces disposes of all of the effluent produced. This system has the added benefit of producing a valuable by-product, as the fast growing poplar and willow in the tree farm could be harvested as an energy crop every few years.

Capital and operating costs, and benefits of each system are outlined and a present worth analysis covering a 20-year period is performed as part of the analysis.

Pre-Feasibility Study on Expansion and Upgrading Of Port Dover Water Pollution Control Plant

M. Kelleher - MacLaren Engineers Inc., Toronto
and
C.S. Papadopol - Ministry of Natural Resources,
Ontario Tree Improvement and
Forest Biomass Institute,
Maple, Ontario

ABSTRACT

The existing Port Dover Water Pollution Control Plant is a primary plant with phosphorus removal and has been subject to a number of operating problems during the last few years. A Study was commissioned to review these problems and evaluate a number of options for expanding and upgrading the plant to provide secondary treatment.

Six options were considered, namely:

- Conventional Activated Sludge
- Rotating Biological Contactors
- Biological Aerated Filters
- Sequencing Batch Reactors
- Extended Aeration, and
- Tree Farm

Capital and operating costs were developed for each option, and a present worth analysis covering a 20-year period was performed. The tree farm, the sequencing batch reactor and the biological aerated filter were the options with least cost over a twenty year period. All of these are innovative technologies, none of which have been implemented on a large scale in Ontario. Pilot testing of each system would be recommended prior to final design.

Pre-Feasibility Study on Expansion and Upgrading Of Port Dover Water Pollution Control Plant

M. Kelleher - MacLaren Engineers Inc.
and
G.C. Papadopol - Ministry of Natural Resources,
Ontario Tree Improvement and Forest
Biomass Institute, Maple, Ontario

INTRODUCTION

The Town of Port Dover is located within the Region of Haldimand-Norfolk, and on the north shore of Lake Erie, and has a population of approximately 3,900. The existing water pollution control centre is located at the east end of the Town, close to the lake. The plant was constructed in 1963 as a primary plant with an average capacity of 9,490 m^3/d (2.09 mIgd), and peak design flows of 18,960 m^3/d (4.2 mIgd). The primary clarifiers were later downrated to provide phosphorus removal by addition of ferric chloride, and the design flow was revised to 4090 m^3/d (0.9 m Igd). Raw primary sludge is stored in a holding tank, and is lime stabilized prior to removal off site, which occurs twice per week. The sludge is applied directly to agricultural land, but if land is not available for direct sludge application, it is temporarily stored in a lagoon located in a rural area some distance from the water pollution control centre. There have been a number of complaints regarding odours from these lagoons, hence a more satisfactory method of sludge stabilization is required.

Port Dover is one of the few remaining primary plants on the Great Lakes. This Study was initiated to investigate methods of upgrading the existing plant to provide secondary treatment, and also to recommend a more acceptable method of sludge treatment and disposal.

Six options were considered, five involving expansion at the existing plant, and the sixth involving spray irrigation of a tree farm located some distance from the existing treatment plant. Considerable input on the design of the tree farm was received from the Ministry of Natural Resources staff. MacLaren Engineers Inc. were responsible for the engineering aspects of the study.

Design Flow and Quality

The Region of Haldimand-Norfolk has a current population of 88,000, which is projected to increase to 102,700 by the year 2007. In this time, it is expected that the population of Port Dover will increase to 5,500.

Daily flows to the plant during the last five years were analysed to develop typical average, dry weather and wet weather flow rates and peaking factors. These were then applied to the future design population and development areas, and resulted in the following design flows for the expansion:

Average	4,040 m^3/d
Peak	14,350 m^3/d

The average influent quality to the plant during the last five years has been BOD 189 mg/L, SS 256 mg/L and P 7 mg/L. Designs were developed assuming a 15:15:1 effluent would be required.

Existing Facilities, and Capacity for Future Flows

The existing plant contains an aerated grit chamber, three primary clarifiers and a chlorine contact chamber. Effluent is discharged through a 600 mm diameter outfall pipe, which terminates in an outfall crib structure located in an average depth of 4.4 m of water, approximately 760 m off shore.

The aerated grit chamber, chlorine contact chamber and outfall all have adequate capacity for future flows. The existing primary clarifiers have adequate capacity for future flows if phosphorus removal does not occur in these tanks, however, if phosphorus removal takes place in the primaries (which is the case for one of the design options), a fourth tank of similar dimensions is required.

Expansion Considerations

The existing plant occupies a small section of a property located outside the built-up part of Port Dover, at the east end of the town. There is adequate area for expansion at the plant, however, a school is located on the adjacent property to the west, and a residential subdivision is located on the adjacent property to the east, hence, expansion at the existing plant is liable to be a sensitive issue.

Options Considered

Six options were considered for expansion/upgrading of the plant, namely:

- Conventional Activated Sludge
- Rotating Biological Contactors
- Biological Aerated Filters

- Sequencing Batch Reactors
- Extended Aeration, and
- Tree Farm

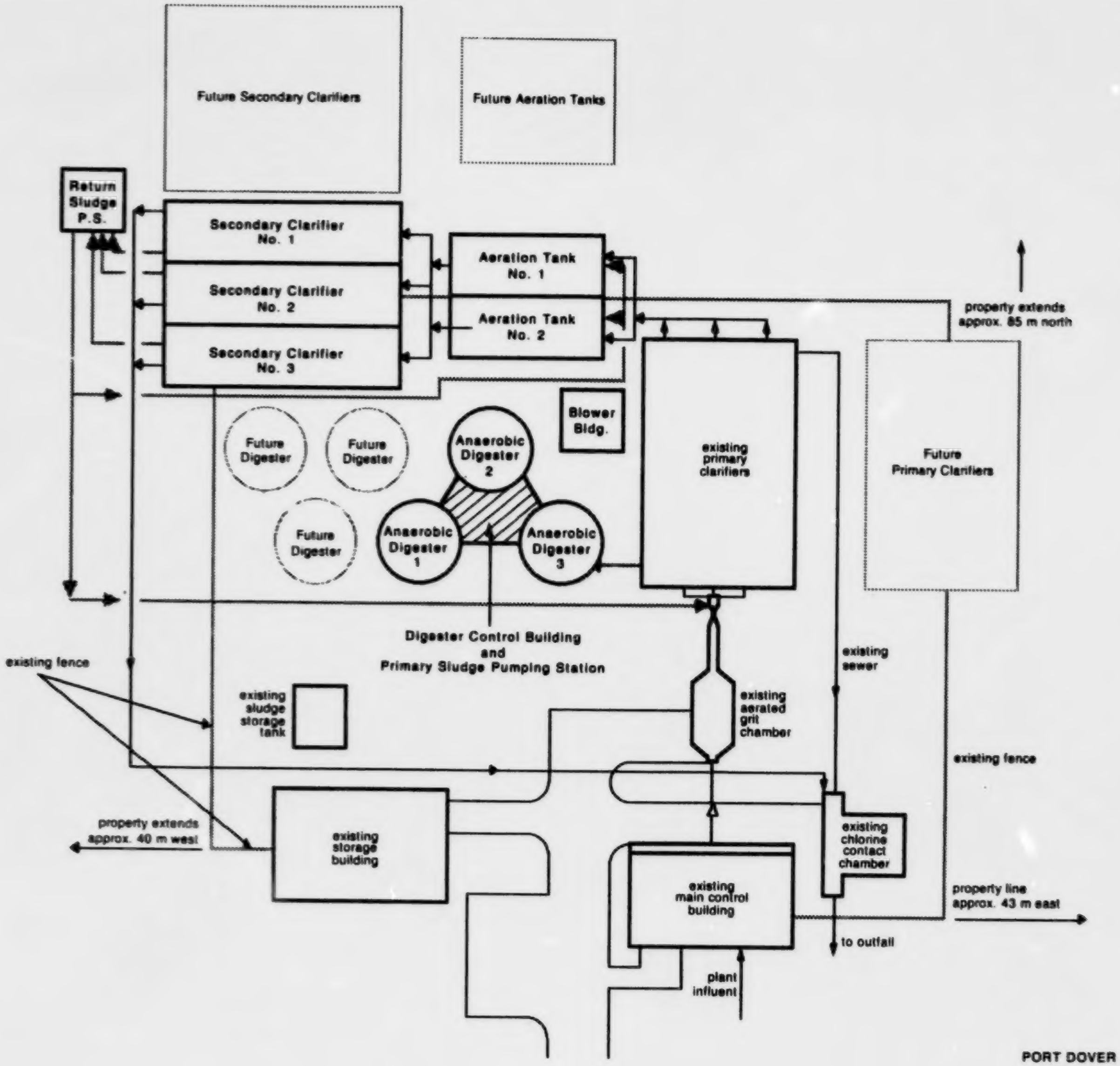
Of these, the first five would be located at the existing plant, and the sixth would be located remote from the existing plant.

Design Approach - Secondary Treatment Options

Designs were developed for the first five options assuming a 15:15:1 effluent requirement. Layouts for each of these options are presented in Figures 1 to 5. Where primary clarification was retained as part of the process train (i.e. for the first three options) it was assumed that sludge would be digested anaerobically. Where primary clarification was eliminated from the process train, as was the case for the Extended Aeration and the Sequencing Batch Reactor designs, it has been assumed that aerobic digestion of sludge would be implemented. In all cases, it was assumed that digested sludge would be hauled off-site and spread on agricultural land.

Conventional Activated Sludge

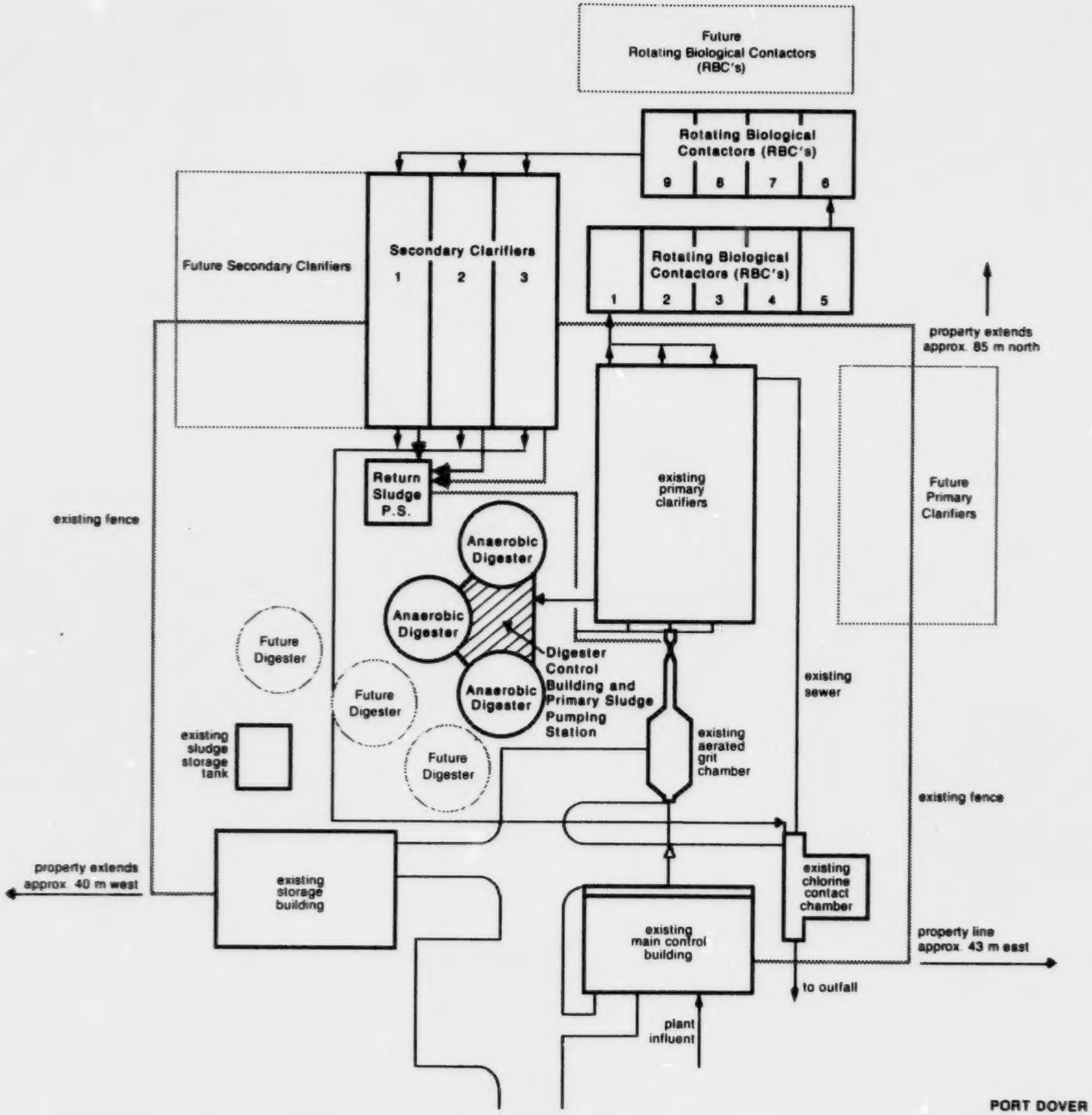
The conventional activated sludge design was developed using MOE criteria. Two aeration basins, each measuring 17 m x 7.5 m x 4 m s.w.d. would be required. This would provide 6.1 hours retention at average flows. Three secondary clarifiers were recommended to provide greater operational flexibility. Phosphorus removal would be accomplished in the secondary clarifiers. A total clarification area of 396 m^2 would be required, to provide a solids loading rate of 151 $kg/m^2.d$ at peak flow conditions.


Future Secondary Clarifiers
Future Aeration Tanks
Return Sludge P.S.
Secondary Clarifier No. 1
Secondary Clarifier No. 2
Secondary Clarifier No. 3
Aeration Tank No. 1
Aeration Tank No. 2
property extends approx. 85 m north
Future Digester
Future Digester
Future Digester
Anaerobic Digester 2
Anaerobic Digester 1
Anaerobic Digester 3
Blower Bldg.
existing primary clarifiers
Future Primary Clarifiers
Digester Control Building and Primary Sludge Pumping Station
existing fence
existing sludge storage tank
existing aerated grit chamber
existing sewer
existing fence
property extends approx. 40 m west
existing storage building
existing main control building
existing chlorine contact chamber
property line approx. 43 m east
to outfall
plant influent

PORT DOVER SEWAGE TREATMENT STUDY

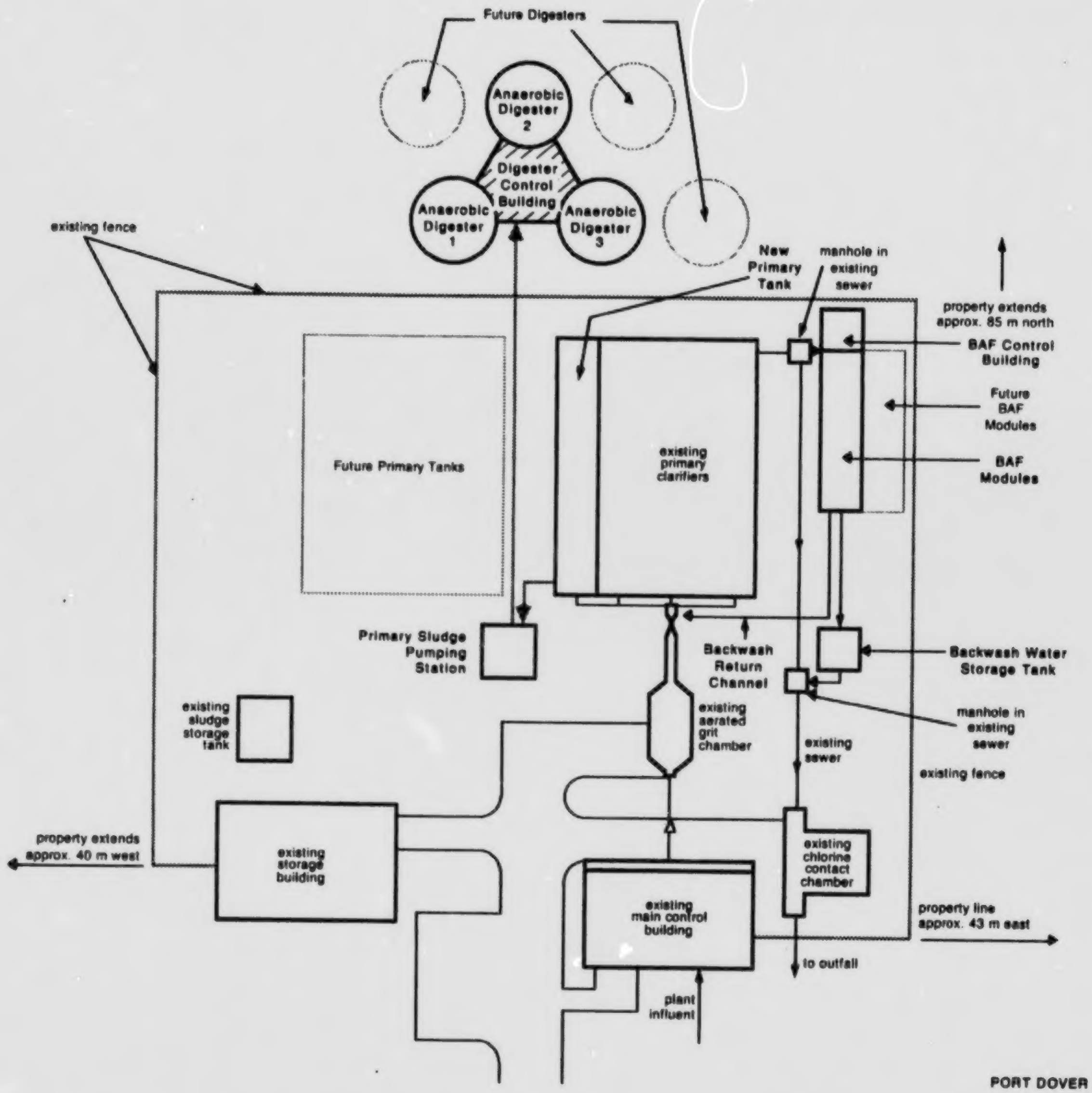
Figure 1

Conventional Activated Sludge Layout


Future
Rotating Biological Contactors
(RBC's)
Rotating Biological Contactors (RBC's)
9
8
7
6
Rotating Biological Contactors (RBC's)
1
2
3
4
5
Future Secondary Clarifiers
Secondary Clarifiers
1
2
3
property extends approx. 85 m north
Return Sludge P.S.
existing primary clarifiers
Future Primary Clarifiers
existing fence
Anaerobic Digester
Anaerobic Digester
Anaerobic Digester
Future Digester
Future Digester
Future Digester
Digester Control Building and Primary Sludge Pumping Station
existing sewer
existing sludge storage tank
existing aerated grit chamber
existing fence
property extends approx. 40 m west
existing storage building
existing chlorine contact chamber
existing main control building
property line approx. 43 m east
to outfall
plant influent

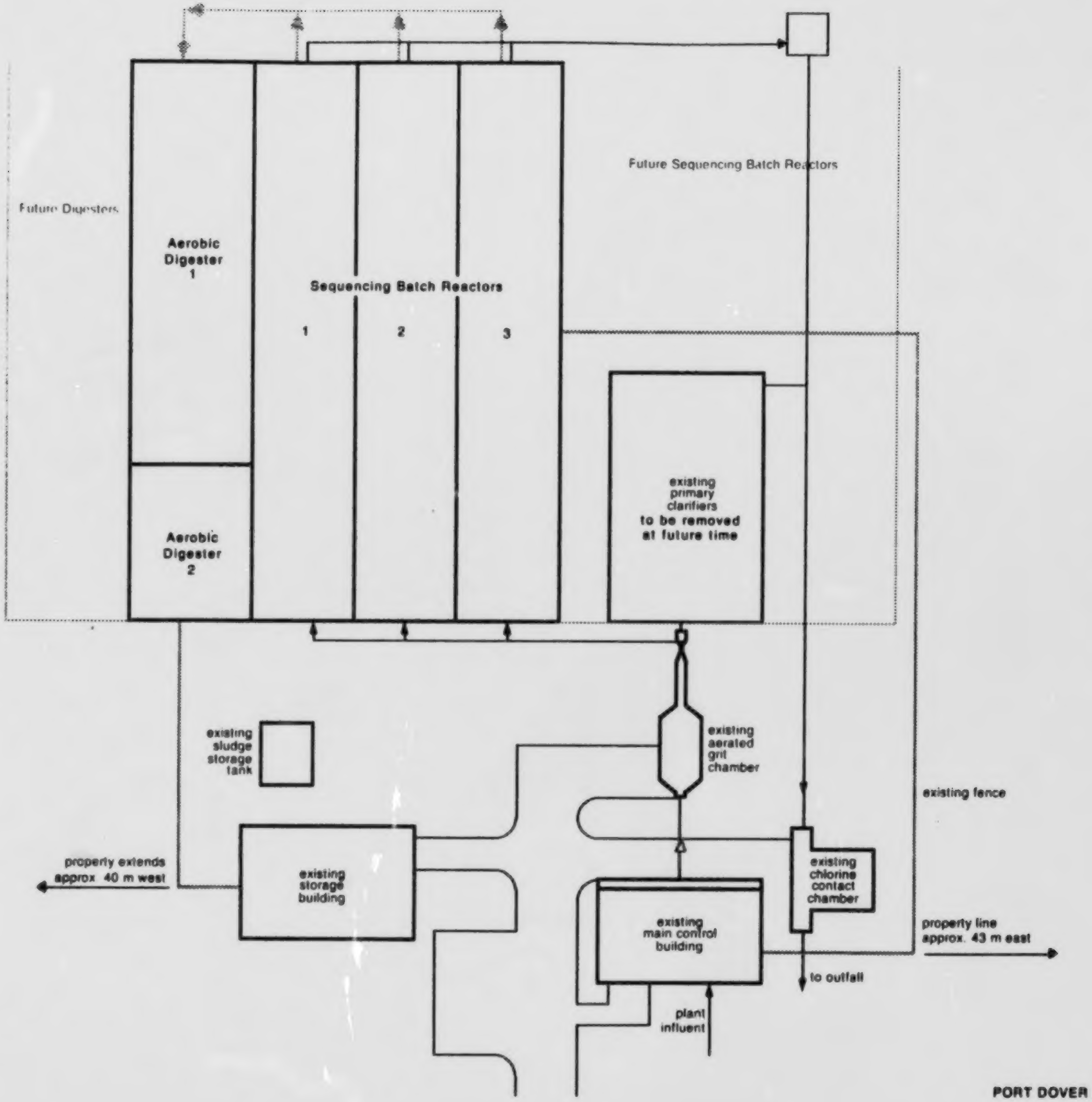
PORT DOVER SEWAGE TREATMENT STUDY

Figure 2
Rotating Biological Contractors Layout


Future Digesters
Anaerobic Digester 2
Digester Control Building
Anaerobic Digester 1
Anaerobic Digester 3
existing fence
New Primary Tank
manhole in existing sewer
property extends approx. 85 m north
BAF Control Building
Future BAF Modules
BAF Modules
Future Primary Tanks
existing primary clarifiers
Primary Sludge Pumping Station
Backwash Return Channel
Backwash Water Storage Tank
manhole in existing sewer
existing sludge storage tank
existing aerated grit chamber
existing sewer
existing fence
existing chlorine contact chamber
property extends approx. 40 m west
existing storage building
existing main control building
property line approx. 43 m east
to outfall
plant influent

PORT DOVER SEWAGE TREATMENT STUDY

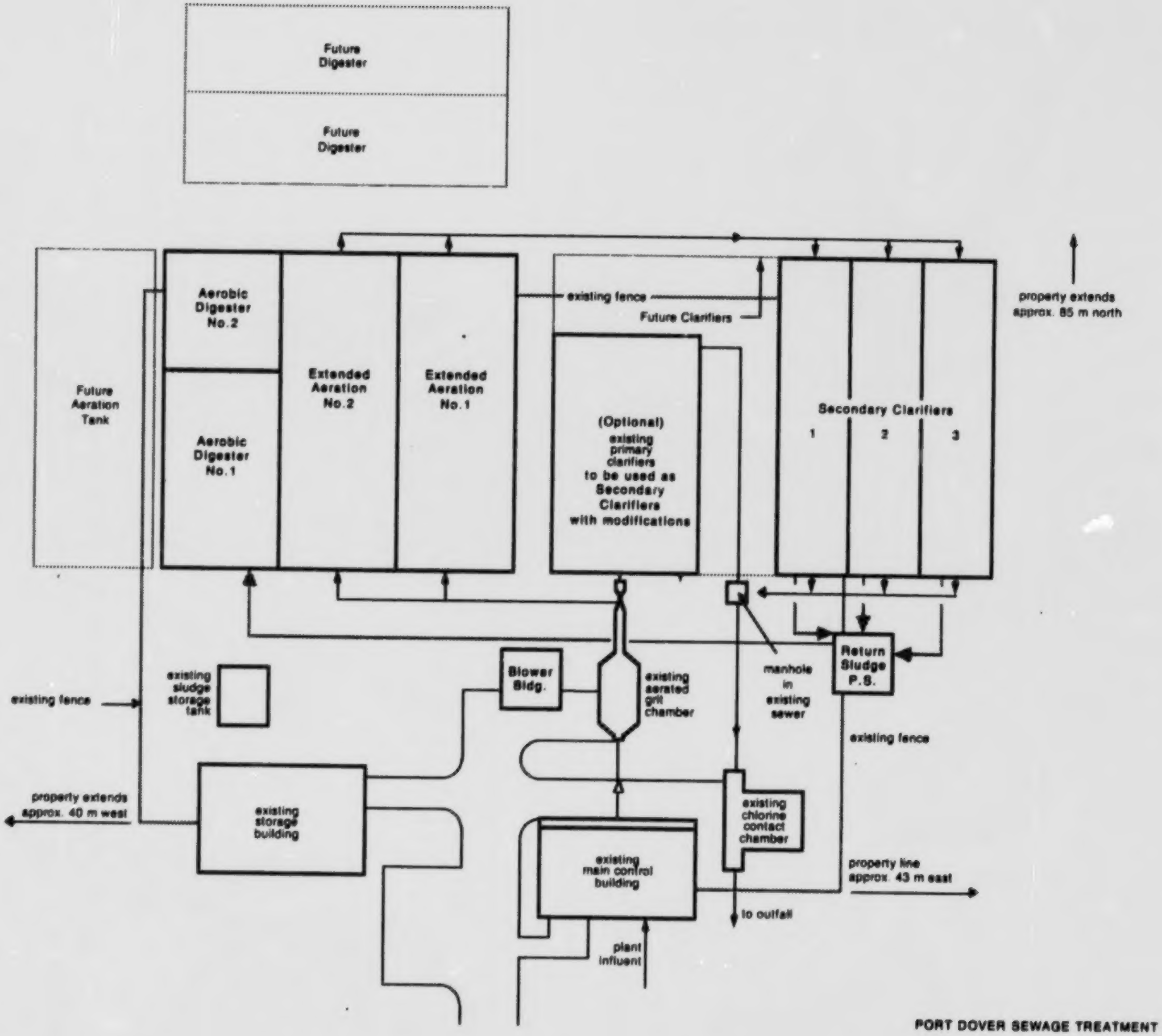
Figure 3
Biological Aerated Filter Layout


Future Digesters
Aerobic Digester 1
Aerobic Digester 2
Sequencing Batch Reactors
1
2
3
Future Sequencing Batch Reactors
existing primary clarifiers to be removed at future time
existing sludge storage tank
existing aerated grit chamber
existing fence
existing storage building
existing chlorine contact chamber
existing main control building
property extends approx 40 m west
property line approx. 43 m east
to outfall
plant influent

PORT DOVER SEWAGE TREATMENT STUDY

Figure 4

Sequencing Batch Reactor Layout


Future Digester
Future Digester
Future Aeration Tank
Aerobic Digester No.2
Aerobic Digester No.1
Extended Aeration No.2
Extended Aeration No.1
existing fence
Future Clarifiers
(Optional) existing primary clarifiers to be used as Secondary Clarifiers with modifications
Secondary Clarifiers
1
2
3
property extends approx. 85 m north
existing sludge storage tank
existing fence
Blower Bldg.
existing aerated grit chamber
manhole in existing sewer
Return Sludge P.S.
existing fence
existing storage building
property extends approx. 40 m west
existing chlorine contact chamber
existing main control building
property line approx. 43 m east
to outfall
plant influent

PORT DOVER SEWAGE TREATMENT STUDY

Figure 5
Extended Aeration Layout

Rectangular clarifiers were considered at this stage, because they would be more compact than circular units. This was considered desirable due to the proximity of a residential development.

Anaerobic digestion of sludge would be recommended because primary sludge is produced in this design option. Three 10 m diameter digesters would be recommended, to provide more operational flexibility. The digesters were sized to provide a 15 day hydraulic retention time, using tYpical sludge production figures for conventional activated sludge plants, provided in the MOE Guidelines.

Rotating Biological Contactors

Preliminary design of the RBC system was carried out by Napier-Reid, to whom influent and effluent qualities and future flows were provided. RBC systems are designed on the basis of both hydraulic and organic loading rates, and the system recommended for Port Dover consisted of four standard density shafts and one high density shaft each 7.6 m long, and 3.6 m diameter. These would be contained in one concrete tank, with baffle walls separating the different RBC compartments. A fibre reinforced plastic (FRP) cover would be installed over each shaft. The design assumed a mechanically driven system, although air driven systems could also be considered. The secondary clarifiers and anaerobic digesters would be similar to the conventional activated sludge design.

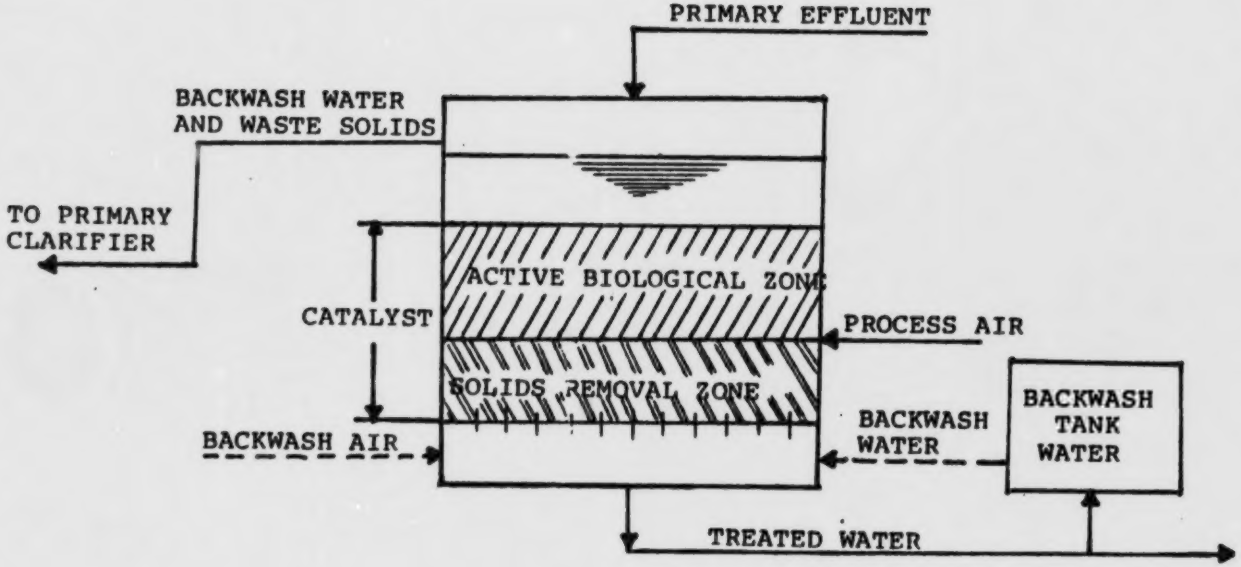
Biological Aerated Filter

The Biological Aerated Filter is a relatively new treatment approach, marketed exclusively by Envirotech in Canada. It consists of a steel tank filled with fired clay media. As shown in Figure 6 effluent is introduced at the top of the media, the upper section of which accomplishes biological treatment, and the lower section of which acts as a clarifier. Solids are removed from the BAF system by periodic (usually 24-hour) backwash, and are returned to the plant headworks. The major advantage of this system is the low space requirement, and the fact that no secondary clarifiers are required, thus saving considerable capital cost.

Primary clarification is required upstream of the BAF module, and phosphorus removal must be accomplished in the primary tank. For this reason, an additional primary clarifier measuring 21.7 m x 4.6 m x 3 m s.w.d. would be required at Port Dover. Design of the BAF system was carried out by Envirotech, who recommended a BAF system measuring 3.7 m x 3.7 m x 19.2 m long, and containing nine cells. This is approximately the same size as one of the existing primary tanks, which illustrates the compact nature of the design. Anaerobic digestion of sludge in three 10 m diameter digesters would be recommended.

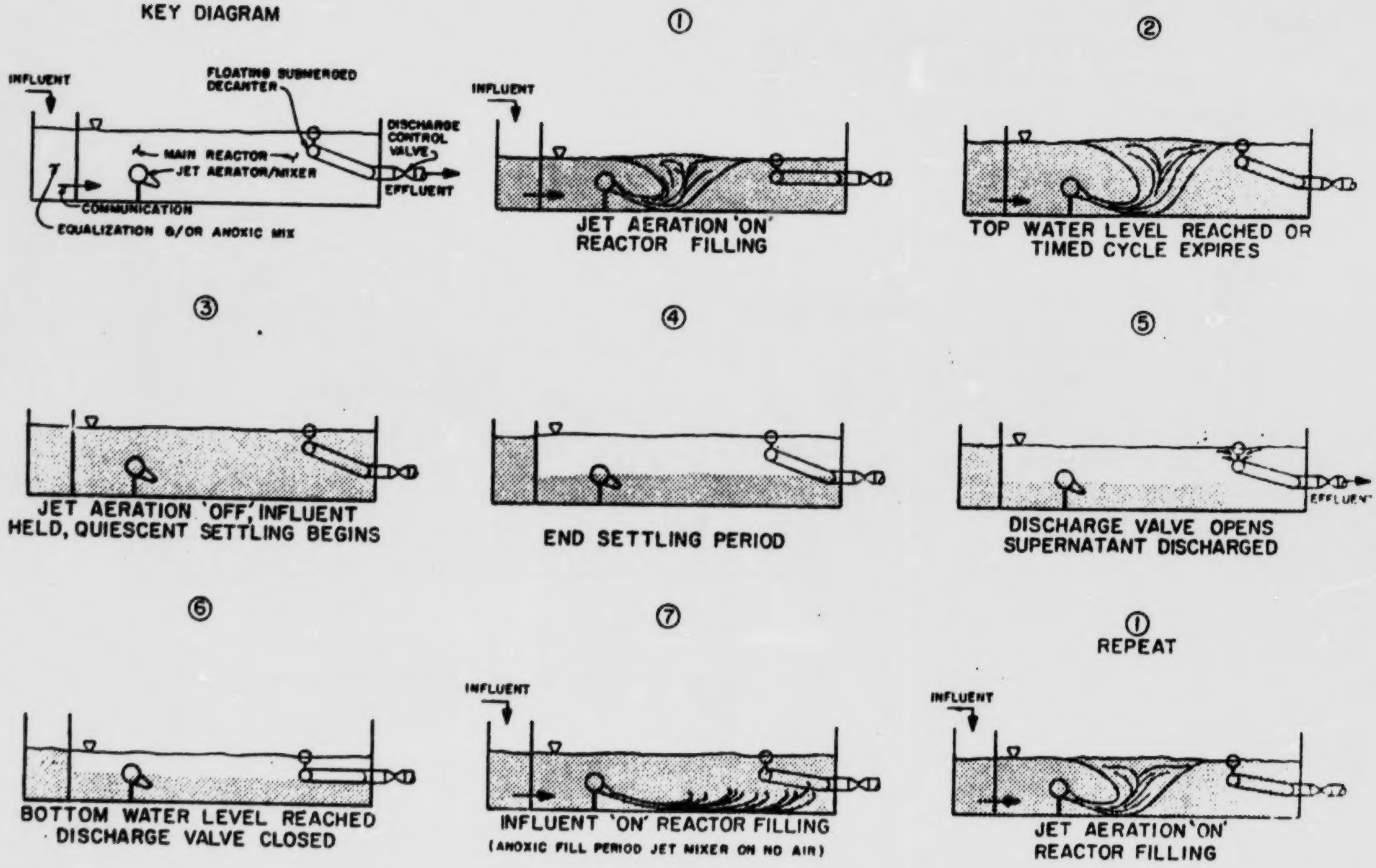
Sequencing Batch Reactors

A sequencing batch reactor is an activated sludge system operating in a batch mode. Each cycle consists of a fill period,an aeration period, a settling period and a discharge period, as shown on Figure 7. The length of each period, and operation of the system will vary from one location to another. This treatment system has become popular in recent years with the advent of microprocessors, which simplify control and operation of the system.


PRIMARY EFFLUENT
BACKWASH WATER AND WASTE SOLIDS
TO PRIMARY CLARIFIER
ACTIVE BIOLOGICAL ZONE
CATALYST
PROCESS AIR
SOLIDS REMOVAL ZONE
BACKWASH TANK WATER
BACKWASH WATER
BACKWASH AIR
TREATED WATER

PORT DOVER SEWAGE TREATMENT STUDY
BIOLOGICAL AERATED FILTER
OPERATIONAL SCHEMATIC

FIG. 6


KEY DIAGRAM
INFLUENT
FLOATING SUBMERGED DECANTER
DISCHARGE CONTROL VALVE
MAIN REACTOR
JET AERATOR/MIXER
EFFLUENT
COMMUNICATION
EQUALIZATION &/OR ANOXIC MIX
①
INFLUENT
JET AERATION 'ON' REACTOR FILLING
②
TOP WATER LEVEL REACHED OR TIMED CYCLE EXPIRES
③
JET AERATION 'OFF', INFLUENT HELD, QUIESCENT SETTLING BEGINS
④
END SETTLING PERIOD
⑤
EFFLUENT
DISCHARGE VALVE OPENS SUPERNATANT DISCHARGED
⑥
BOTTOM WATER LEVEL REACHED DISCHARGE VALVE CLOSED
⑦
INFLUENT
INFLUENT 'ON' REACTOR FILLING
(ANOXIC FILL PERIOD JET MIXER ON NO AIR)
① REPEAT
INFLUENT
JET AERATION 'ON' REACTOR FILLING

PORT DOVER SEWAGE TREATMENT STUDY
SEQUENCING BATCH REACTOR
OPERATIONAL SCHEMATIC

FIG. 7

Design of an SBR system for Port Dover was provided by Jet Tech Inc. of Kansas City, who recommended two SBR tanks, each with a volume of 1515 m^3, which would operate on four cycles a day under normal conditions. Phosphorus removal would be achieved biologically in the SBR tanks, and primary sedimentation would be eliminated from the process train, as only fine screening of raw sewage is required ahead of this system.

Aerobic digestion of sludge would be recommended. It was assumed that 57 m^3/d of sludge would be produced by this system, and that a 5 day sludge age would be provided in the SBR tanks, therefore a 40 day residence time would be required in the digestion system, to provide the total 45 day sludge age recommended by MOE. On this basis, two digesters, the first 34 m x 11.2 m x 4 m s.w.d., and the second measuring 16.5 m x 11.2 m x 4 m s.w.d. would be recommended.

Extended Aeration

This system was considered for Port Dover, as it is relatively easy to operate, and is considered appropriate for this size of plant. Two aeration tanks, each measuring 32 m x 12.5 m x 4 m s.w.d. and providing a detention time of 19 hours at average flow would be recommended. Secondary clarifiers following extended aeration are designed on a very conservative basis, hence, using the MOE criterion of a solids loading rate of 120 $kg/m^2.d$ at peak flow conditions, three rectangular clarifiers, each measuring 32 m x 7.1 m x 4 m s.w.d. would be recommended. The possibility of using the existing primary tanks as secondary clarifiers to provide approximately 40% of the required clarification capacity was considered, however, the cost savings were not significant, and the treatment results from the shallower tanks might not be acceptable, hence new clarifiers would be preferable.

As the existing primary tanks would be eliminated from the process train, and no primary sludge would be produced, aerobic digestion of sludge would be recommended. Two digesters, measuring 20 m x 12.5 m x 4 m s.w.d. and 12 m x 12.5 m x 4 m s.w.d. and providing a total of 30 days retention, would be required. These were sized using typical sludge quantities provided in the MOE Guidelines, and assuming that a 15 day sludge age would be provided in the extended aeration system, hence the digestion system should provide an additional 30 day retention time.

Tree Farm

This is a novel concept whereby Port Dover Sewage would be disposed of by irrigation of a tree farm. The leaf surfaces would provide a large area from which effluent would evaporate and nutrients would be taken up by the tree root system. This treatment option would have a number of advantages for Port Dover. Discharge of effluent to Lake Erie would be discontinued, and nutrients would be recycled by uptake through the tree root system. A useful end product, which could be marketed as an energy crop would be produced, and the existing treatment plant could be closed, and operated as a pumping station only. Extensive work was carried out on this aspect of the study by Ministry of Natural Resources staff at the Ontario Tree Improvement and Forest Biomass Institute, in Maple, Ontario, who recommend that such a tree farm be designed for spray irrigation on 120 days per year, and that an area of 200 ha be used for preliminary design purposes. The trees would be hybrid poplar and some willow in wet areas, planted in a 4 m x 4 m grid, which would result in 625 trees/hectare.

The tree farm option would consist of a number of components, namely:

(a) Pumping Station and forcemain to deliver sewage to tree farm location.

(b) Lagoons, for storage of sewage through winter and days when spray irrigation is not possible.

(c) Underdrainage system to drain storm runoff and snowmelt.

(d) Spray irrigation system, including spray nozzles, distribution piping and pumps.

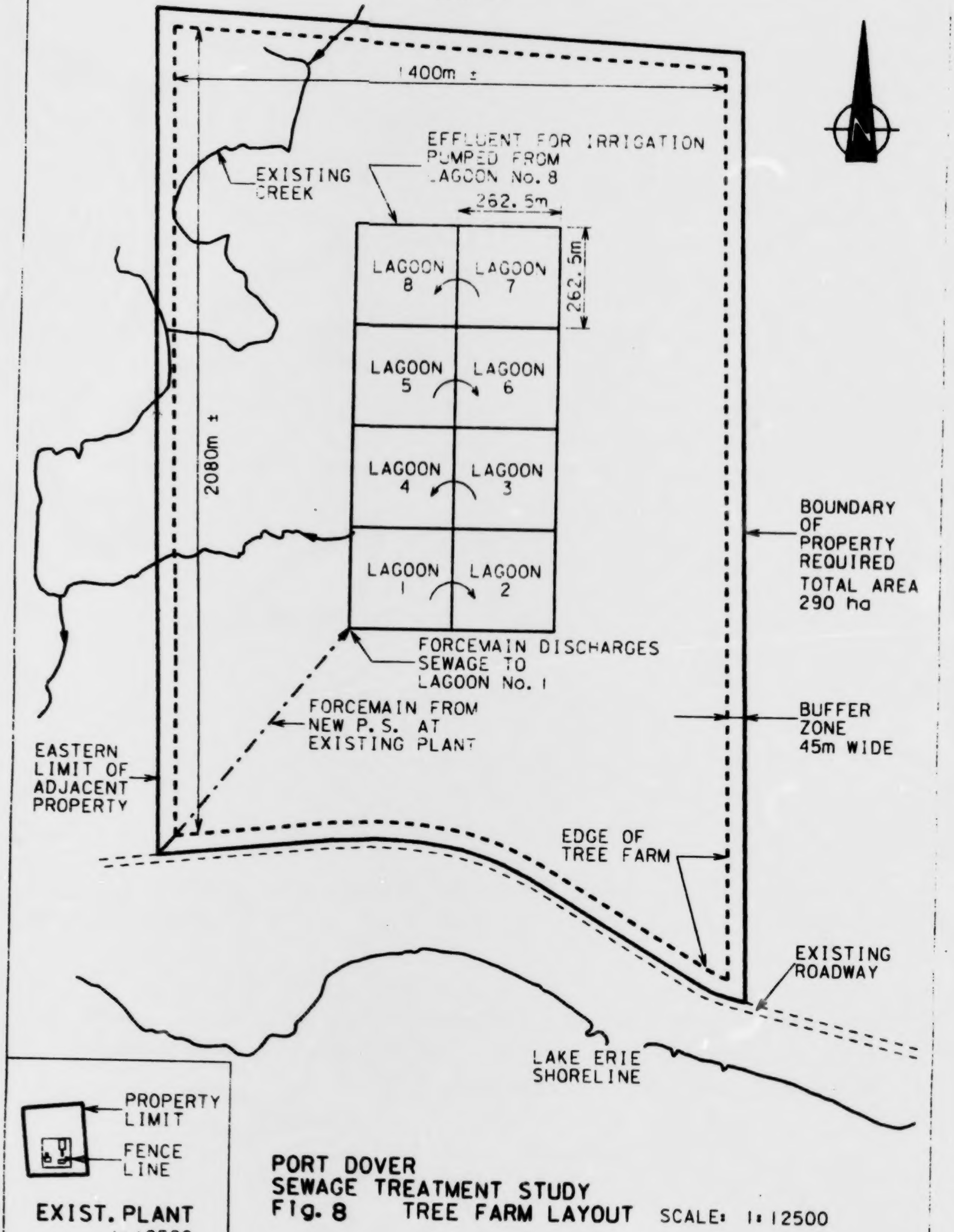
(e) Small control building.

A preliminary layout is presented in Figure 8.

The pumps and forcemain were designed assuming that the tree farm would be located within 5 km of the existing plant, and at a similar elevation.

The lagoons were sized for 245 days storage at a depth of 1.8 m, hence eight lagoons, each 6.9 ha in area would be recommended.

The underdrainage system would consist of typical farm drainage piping for the Port Dover area, usually 75 mm to 100 mm diameter pipe, at 6 m spacing.


1400m ±
2080m ±
EXISTING CREEK
EFFLUENT FOR IRRIGATION PUMPED FROM LAGOON No. 8
262.5m
262.5m
LAGOON 8
LAGOON 7
LAGOON 5
LAGOON 6
LAGOON 4
LAGOON 3
LAGOON 1
LAGOON 2
FORCEMAIN DISCHARGES SEWAGE TO LAGOON No. 1
FORCEMAIN FROM NEW P.S. AT EXISTING PLANT
EASTERN LIMIT OF ADJACENT PROPERTY
BOUNDARY OF PROPERTY REQUIRED
TOTAL AREA 290 ha
BUFFER ZONE 45m WIDE
EDGE OF TREE FARM
EXISTING ROADWAY
LAKE ERIE SHORELINE
PROPERTY LIMIT
FENCE LINE
EXIST. PLANT
1:12500

PORT DOVER
SEWAGE TREATMENT STUDY
Fig. 8 TREE FARM LAYOUT SCALE: 1:12500

Comparison of Options

Capital and operating costs for each option are provided in the attached tables 1, 2 and 3. Capital costs of the options are self explanatory. The components of the operating costs for the various options vary considerably, depending on their labour, power and chemical requirements. Therefore, options such as extended aeration and sequencing batch reactors, which are relatively easy to operate, and therefore have a low labour requirement, have high power costs because of the aeration requirements of the aerobic digestion system and the aeration tanks. Sludge disposal costs for these options are also high, because of the larger volumes of sludge involved. Chemical costs for the SBR are low because phosphorus removal is accomplished biologically in the aeration tanks.

The major advantages of the tree farm become apparent at this time, as its operation is significantly less costly than operation of any of the other systems. The power costs for this system are related to pumping sewage to the lagoons, and operating the spray irrigation system for 10 hours per day, 120 days per year.

The Present Worth Analysis which is the only common basis on which to compare the various options is presented in Table 4. Table 5 presents a summary of the advantages and disadvantages of each option.

The Biological Filter, the Sequencing Batch Reactor and the Tree Farm all compare cost wise, however, if the value of the wood produced by the tree farm is taken into consideration, the tree farm is the most economical option over a twenty year period. Derivation of the value of wood produced is shown in Table 6, and was developed using a Thinning Schedule

TABLE 1

ESTIMATED CAPITAL COSTS OF SECONDARY TREATMENT OPTIONS

Item	Conventional Activated Sludge	Biological Aerated Filter	Rotating Biological Contractor	Extended Aeration	Sequencing Batch Reactor
Primary Tanks	-	300,000	-	-	-
Aeration Tanks	420,000	-	-	840,000	-
Process Tanks & Units	-	700,000	450,000	-	1,600,000
Secondary Clarifiers	1,400,000	-	1,400,000	1,860,000	-
Anaerobic Digesters and Control Bldg.	2,100,000	2,100,000	2,100,000	-	-
Aerobic Digesters	-	-	-	550,000	680,000
Miscellaneous*	140,000	100,000	80,000	160,000	100,000
Sub-Total	4,060,000	3,200,000	4,030,000	3,410,000	2,380,000
Estimating Allowance 15%	610,000	480,000	600,000	510,000	360,000
Total Estimated Cost	4,670,000	3,680,000	4,630,000	3,920,000	2,740,000

* Includes primary sludge and return sludge pumping stations, blower buildings and miscellaneous yard piping.

TABLE 2

ESTIMATED CAPITAL COSTS OF TREE FARM OPTION

Item	Cost
Pumping Station at Existing Plant	160,000
Spray Irrigation System	1,500,000
Underdrainage System	500,000
Lagoons	1,750,000
Forcemain	1,050,000
Establishment Costs	200,000
Control Building	50,000
Sub-total	$5,210,000
Estimating Allowance (15%)	790,000
	$6,000,000*

* Land cost not included.

TABLE 3

ESTIMATED OPERATING COSTS OF TREATMENT OPTIONS

Item	Conventional Activated Sludge	Biological Aerated Filter	Rotating Biological Contractor	Extended Aeration	Sequencing Batch Reactor	Tree Farm
Number of full time employees	4	3.5	3.5	2.5	2.5	2.0
Labour	117,200	103,000	103,000	74,600	74,600	60,400
Power	51,300	33,800	41,000	100,000	100,000	61,000
Chemicals	23,500	35,300	23,500	23,500	8,000	1,000
Sludge Haulage*	29,000	29,000	29,000	81,300	85,000	-
Miscellaneous**	31,000	30,400	30,400	26,700	26,400	5,000
Total (In 1985 dollars)	252,000	231,500	226,900	305,800	295,000	127,400

* Based on a cost of $5.50/cubic metre for sludge disposal.

** Includes Miscellaneous Repairs, Maintenance and General Supplies

TABLE 4

PRESENT WORTH ANALYSIS OF OPTIONS

Item	Conventional Activated Sludge	BAF	RBC	Extended Aeration	Sequencing Batch Reactor	Tree Farm	Phased Tree Farm
Capital Cost	4,670,000	3,680,000	4,630,000	3,920,000	2,740,000	6,000,000	6,347,500
Present Worth of 20-year Operating Cost	4,239,400	3,894,200	3,816,900	5,144,000	4,962,000	2,143,000	2,329,500
Present Worth of Capital and Operating Cost	8,909,000	7,574,200	8,446,900	9,064,000	7,702,400	8,143,000	8,677,000
Present Worth of Timber Production	-	-	-	-	-	967,000	882,900
Present Worth of 20-Year Net Cost	8,909,000	7,574,200	8,446,900	9,064,000	7,702,400	7,176,000	7,794,100

TABLE 5

COMPARISON OF OPTIONS

OPTION	ADVANTAGES	DISADVANTAGES
Conventional Activated Sludge	- proven process	- high capital cost - high operating costs - high labour requirement - high energy requirement
Biological Aerated Filter	- compact system - relatively low capital cost - reasonable operating cost - very low space requirements	- new technology - unproven in Canada
Rotating Biological Contactor	- ease of operation - low energy requirement - proven process - reasonable operating cost	- high capital cost
Extended Aeration	- ease of operation - low manpower requirements - reasonable capital costs	- very high energy requirements - large volume of sludge for disposal - high operating costs
Sequencing Batch Rector	- ease of operation - low capital cost - ability to resist shock loads	- high energy requirement - high operating costs - unproven in Canada on this scale - new design approach
Tree Farm	- low manpower requirements - location remote from population - no effluent to Lake Erie - produces useful end product - possible funding for innovative project - low operating costs - existing plant would be closed.	- high energy requirements - unproven process on this scale - large land requirements - high capital cost

TABLE 6

TREE FARM TIMBER PRODUCTION AND VALUE

	Tonnes of Wood Produced*	Value** 1985 $	Present Worth $
Year 6	4,788	184,300	168,200
	2,394‡	92,150‡	84,100‡
Year 10	7,144	275,000	231,900
Year 14	7,144	275,000	214,600
Year 20	13,100	503,300	352,300
Total present worth of Timber Production			$967,000. $882,900‡

* Assuming a density of 380 kg/m³
** Assuming $38.50/tonne.
‡ Phased tree farm

recommended by Ministry of Natural Resources staff. Phasing of the tree farm over a five year period was also recommended, but not absolutely essential. Even when the tree farm is phased, the economics are favourable when compared to the other options.

Summary and Conclusions

Six preliminary designs were developed for upgrading and expansion of the Port Dover Water Pollution Control Centre. Five options involved expansion at the existing plant location. The sixth option involved relocating the treatment facilities to an area remote from the existing plant, and developing a tree farm in this area for spray irrigation of effluent. A preliminary design and cost estimate was carried out for each option, and operating costs estimated. A 20-year present worth analysis was carried out, to provide a common basis on which to evaluate the options. The Biological Aerated Filter, the Sequencing Batch Reactor and the Tree Farm Options are the most economical of those considered. If the value of the wood produced by the tree farm is taken into consideration, it is the most economical of the options over a 20-year life span.

The three options under consideration should be evaluated in greater detail. Pilot testing of the Biological Aerated Filter and the Sequencing Batch Reactor, and hydrogeological and soil testing of the potential tree farm location would be recommended.

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THE EFFECTS OF WASTEWATER QUALITY ON ULTRAVIOLET LIGHT DISINFECTION

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Key words: Wastewater Quality, Sewage Treatment, Disinfection, Ultraviolet Light Irradiation.

ABSTRACT

Although the ultraviolet light irradiation of treated wastewater has been accepted as a disinfection method, many of the effects of wastewater quality on this process have not been studied at the full scale level.

A full scale gravity flow UV system was placed in the effluent channel of a conventional secondary wastewater treatment plant. The system consisted of a series of modules forming two separate rectangular matrices of UV lamps.

Disinfection is a function of the intensity of UV light and the time of irradiation. The intensity is determined by the lamp output and the UV transmission of the effluent. A UV absorbing compound will be added to the effluent to determine the effect of intensity on disinfection efficiency before and after photoreactivation and will also determine when the UV lamps should be replaced. These experiments will verify that the UV sensor responds linearily to UV transmission. The response of the sensor will then be verified by using the various mathematical models which predict UV intensity and dosage.

The effect of suspended solids in primary and secondary solids may have the most significant effect on the efficiency of disinfection due to the protection of bacteria from UV light. Varying amounts of the three effluents will be mixed with high quality secondary effluent to determine the bacterial reductions before and after photoreactivation. These experiments will be repeated at the mid-point and end point of lamp life to establish the effective lamplife for different qualities of wastewater.

Photoreactivation accounts for the greatest increase in bacterial numbers after UV disinfection. The effect of UV transmission and/or suspended solids on this phenomenon will be studied. The irradiated bacteria will be exposed to various stream conditions and sunlight while they are in glass bottles and an irradiated tracer organism will be exposed to the sunlight and the receiving stream at the same time.

This study will determine whether a correlation exists between *E. coli* or bacteriophage and the pathogens which may remain in the UV disinfected wastewater. Bacteriophage can be enumerated in as little as four hours and this would serve as a rapid indicator of UV disinfection.

The current mathematical models' ability to predict the dosages within this UV reactor will be compared to actual bacterial reductions to develop design criteria for the UV reactor and various wastewaters.

The Effects of Wastewater Quality on Ultraviolet Light Disinfection

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The most widely accepted alternative technology to chlorine as a disinfectant in North America for wastewater has been ultraviolet light (UV). White et al. (1985) identified 35 municipal wastewater treatment facilities being designed with UV disinfection, 31 that were under construction, and 52 that were in operation. Of these 118 systems, only 24 included some form of filtration prior to disinfection. Average design flows ranged from 1.9×10^5 m^3/d to 2.7 m^3/d. The most common form of secondary treatment used in the plants are oxidation ditches (31%), the activated sludge process or its variations, extended aeration and contact stabilization (25%). The use of UV irradiation has resulted from research that has shown that residuals of chlorine and chlorinated compounds are harmful to living organisms (Jolley et al., 1978 and 1980; Cairns and Conn, 1979 and Chlorine Objective Task Force, 1980). Chlorine and its related compounds are dangerous to handle and transport. Dechlorination does not remove chlorinated compounds from the effluent. Alternatively, disinfection with UV light does not produce any unwanted residuals in the wastewater and UV light does not have to be transported or handled.

A full scale UV study at the Tillsonburg, Ontario WPCP provided the following information (Whitby et al., 1984). The UV system was able to meet the disinfection requirements of 2500 and 200 total and fecal coliforms per 100 mL respectively after 33 months of total operation. Photoreactivation must be taken into account when UV systems are designed as the fecal and total coliforms increased by 10 fold after exposure to sunlight. UV disinfected effluent was non-lethal to rainbow trout over a 48 hour exposure period. The UV units are more efficient at killing bacteriophage than chlorination. This indicates that UV irradiation may be more effective at eliminating enteric viruses. A cost comparison showed that UV disinfection is cost competitive with other forms of disinfection. UV and chlorine were equally effective at destroying *Pseudomonas*. This was the first side-by-side comparison of UV and chlorine disinfection.

The objectives of this study using the same UV equipment are: to study the effect of soluble UV absorbing compounds on the disinfection process and sensor system; to reduce the effluent quality with primary and secondary solids to determine disinfection efficiency before and after photoreactivation; to determine the degree of photoreactivation and dark repair *in situ* and in the plant at various times of the year and following changes in the levels of the UV transmission and/or solids; to investigate whether a correlation exists between bacteriophage to *Escherichia coli* and indicator and pathogenic bacteria before and after photoreactivation; to correlate UV lamp output and UV sensor readings; and to investigate the various mathematical models of UV intensity dosage etc. versus the measured parameters.

Materials and Methods

Project Site Description

The WPCP is located in Tillsonburg, Ontario, Canada. It is a conventional secondary plant which produces a good quality effluent (Table 1) from primarily domestic sewage. The nature of the effluent allows variables such as UV transmission and suspended solids to be varied over a wide range. The design capacity of the plant is 8.2 X 10^3 m^3/d with an average yearly flow of 4.6 X 10^3 m^3/d.

Description of UV Equipment

The gravity fed UV equipment (Figure 1) consists of a series of modules which are located in the effluent channel directly after the clarifiers. The control equipment is located beside the channel. The wastewater flow is parallel to the UV lamps. The height of the wastewater over the UV lamps is controlled by a gate which opens and closes proportionally to the flow rate. Each UV module has four low pressure mercury lamps which are enclosed in quartz sleeves. Each lamp is 76.2 cm long and under optimum conditions produces 13.8 watts of UV light (manufacturer's literature) at a wavelength of 253.7 nm. Two sets of 10 modules separated by 1.61 metres for a total of 80 lamps are located in the effluent channel which serves half of the total flow of the WPCP. The quartz sleeves are 22 mm in diameter and the centres of the lamps are 60.3 mm apart. All of the UV lamps were new at the start of the research.

UV Light Absorption Experiment

A water soluble compound which only absorbs light in the UV region was added to the effluent to decrease the UV transmission of the wastewater. This method simulated effluents which may contain a soluble UV absorbing compound. To absorb UV light various volumes of a solution containing 5.55 gm/L of parahydroxybenzoic acid (PHB) (Severin, 1982) were metered into the effluent channel upstream of the UV system. The solution of PHB was mixed with the wastewater by bubbling air from a series of pipes on the bottom of the

Table 1. The chemical characteristics of the influent to the UV system during the UV transmission study.

Parameter	Arithmetic Mean	Standard Deviation
%T* 254 nm, 1 cm	77.98	0.47
%T 365 nm, 1 cm	94.3	0.57
DOC	5.2 mg/L	0.30
Apparent Colour (Hazen Units)	15.6	2.5
Turbidity (Formazin Units)	1.79	0.16
pH	7.21	0.09
Conductivity umho/cm^3 at 25°C	1065	45
Iron as Fe	0.06 mg/L	0.17
Free Ammonia	0.2 mg/L	0.1
Total Kjeldahl Nitrogen	0.98 mg/L	0.19
Nitrite	0.04 mg/L	0.01
Nitrate	20.6 mg/L	1.5
Total Phosphorus as P	0.85 mg/L	0.10
Dissolved Reactive Phosphorus as P	0.16 mg/L	0.06
BOD	3.25 mg/L	1.21
Suspended Solids	7.9 mg/L	0.8
Dissolved Solids	710.3 mg/L	22.8
COD	29.6 mg/L	3.9

*Transmission

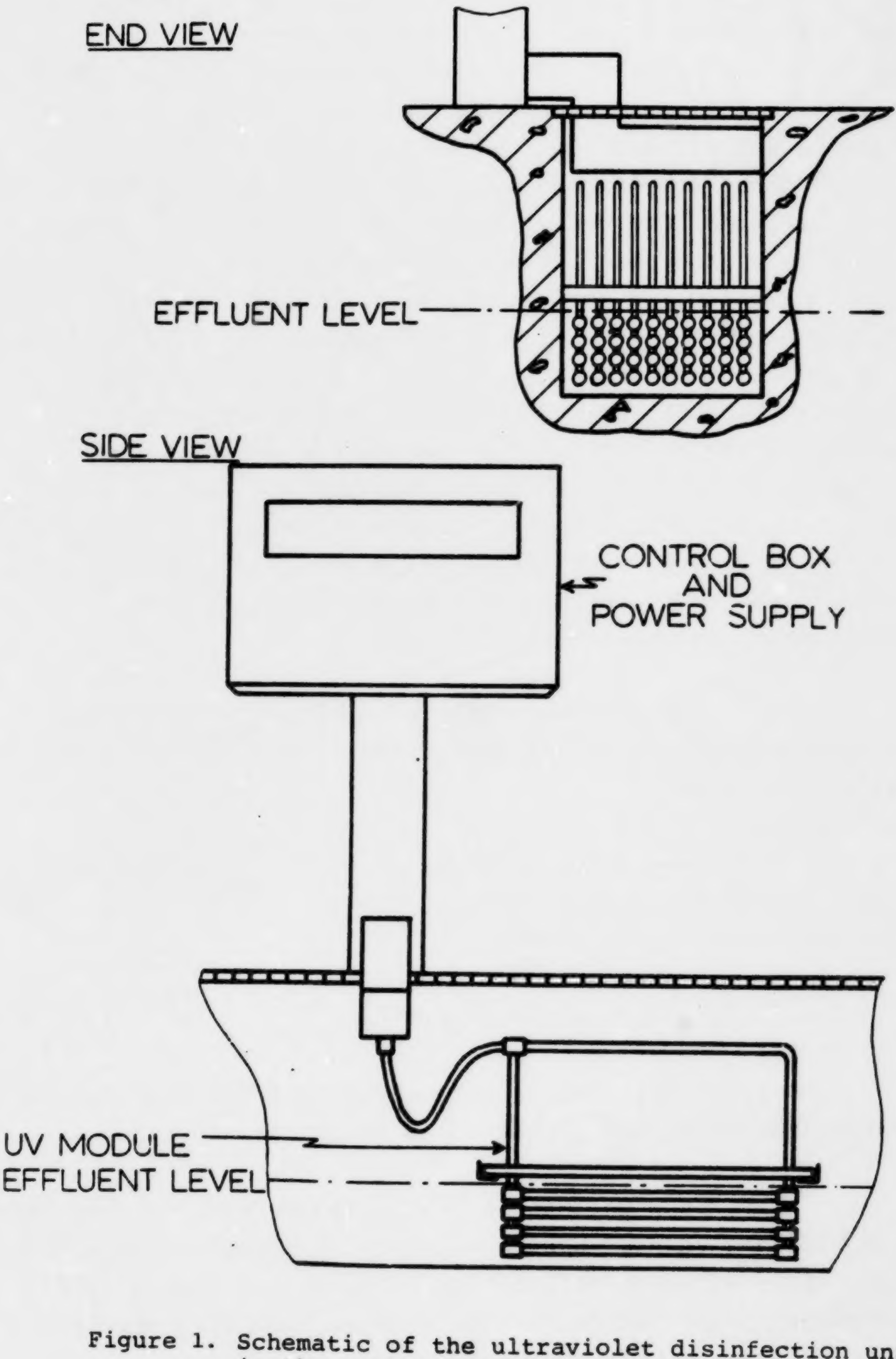
END VIEW
EFFLUENT LEVEL
SIDE VIEW
CONTROL BOX AND POWER SUPPLY
UV MODULE
EFFLUENT LEVEL

Figure 1. Schematic of the ultraviolet disinfection unit in the sewage treatment plant effluent channels.

channel. Samples were taken simultaneously in between the two matrices of UV lamps and after the UV system at the various flow rates of PHB. Control samples without PHB were also taken before, in between, and after the UV system for bacteriological and chemical analysis. The chemical analysis was done according to the Ontario Ministry of the Environment's Handbook of Analytical Methods (Ontario Ministry of the Environment, 1983). One sample from each sampling point was kept in the dark and another was photoreactivated according to the method of Whitby *et al.*, 1984. These samples were analyzed for total and fecal coliforms in the mobile laboratory at the WPCP. Analysis was according to the Ontario Ministry of the Environment's Handbook of Analytical Methods (Ontario Ministry of the Environment, 1983). Another sample was analyzed for UV transmission at a wavelength of 254 nm. The flow rate through the UV equipment was monitored continuously. The experiment was repeated seven times.

A standard curve was prepared of UV transmission at a wavelength of 254 nm versus the concentration of PHB in deionized water.

An absorption spectrum of PHB in deionized water was done for wavelengths between 200 and 700 nm to confirm the work of Severin (1982).

Suspended Solids Experiments

Secondary solids were added to the wastewater to determine the effect of particles on UV disinfection.

Various volumes of return sludge were metered into the effluent channel upstream to the UV system. The solids were mixed with the effluent by bubbling air from a series of pipes on the bottom of the channel. Samples were taken simultaneously before the UV units, in between the two matrices of UV lamps and after the UV system at the various levels of solids. Control samples without added solids were also taken at the sampling points for analysis. One sample from each sampling point, except for the sample before the UV units, was kept in the dark and another was photoreactivated. These samples and the controls were analyzed for fecal and total coliforms. A suspended solids analysis (Ontario Ministry of the Environment, 1983) was carried out for each set of bacteriological samples.

Standard curves were prepared of suspended solids versus transmission of light at wavelengths of 254 nm and 660 nm.

UV Lamp Output Versus Usage

The UV lamps at the WPCP in Tillsonburg had been in continuous use since the spring of 1982. The output of UV light by these lamps had been measured during this time. The UV units at the WPCP were refitted with new lamps at the beginning of this study. The 80 lamps out of the UV system were over 3 years old and these were measured for UV output. Lamps which were burned in for 100 hours were also measured. The output of UV light by the lamps was measured according to the method of Johnson and Qualls (1981).

UV Lamp Output Versus Temperature

The lamp and quartz sleeve combination in the UV system was measured to determine the effect of water temperature on the relative UV output.

The experimental set-up was as shown in Figure 2. The quartz sleeve and lamps which were burned in for 100 hours were identical to that used in the UV unit at the

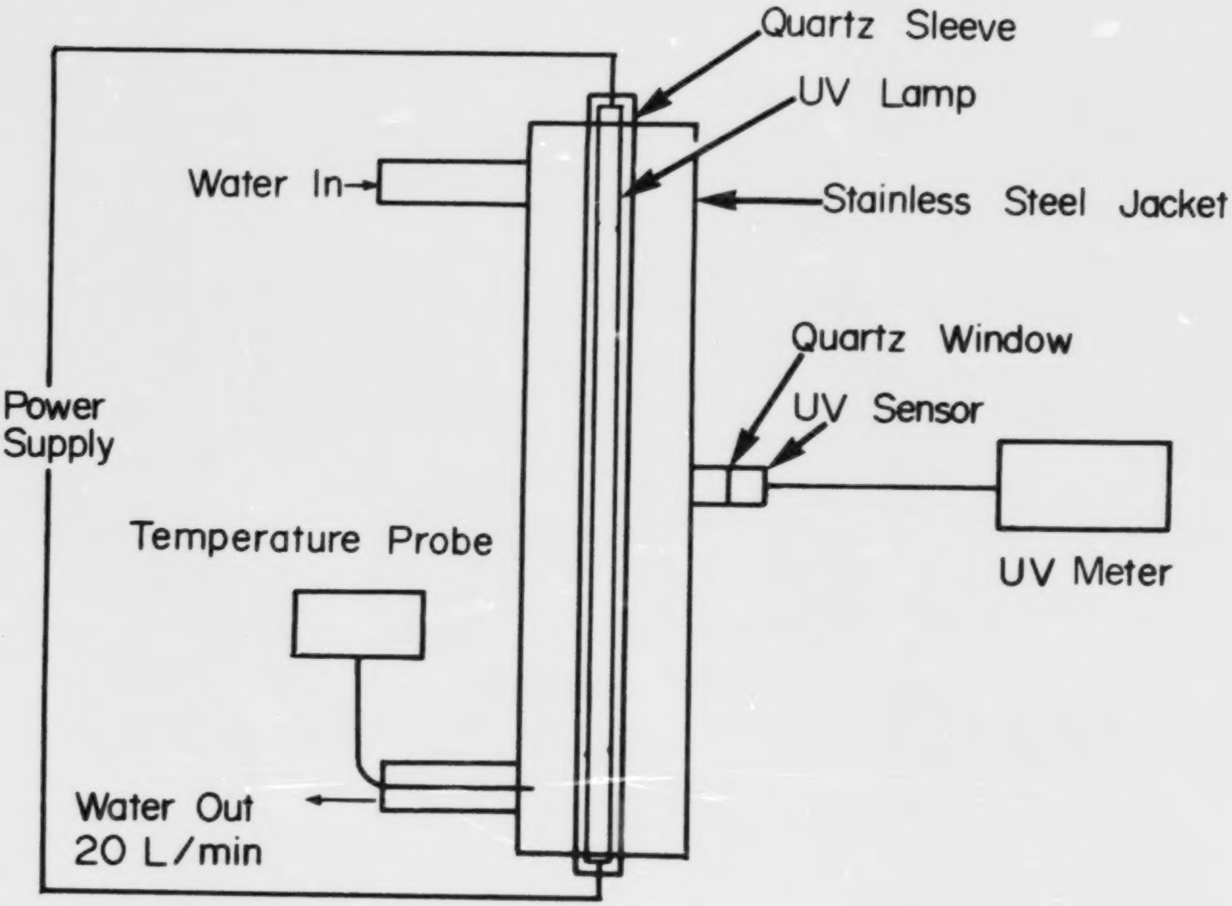
Quartz Sleeve
UV Lamp
Water In
Stainless Steel Jacket
Quartz Window
UV Sensor
Power Supply
UV Meter
Temperature Probe
Water Out
20 L/min

Figure 2. The experiment set-up for measuring the UV output of the quartz sleeve and lamp combination used in the UV system.

WPCP. The relative UV output was measured with an International Light 500 Radiometer and SEE254 probe calibrated to an NBS light standard. UV output readings were taken until a plateau was reached. The temperature of the water was varied from 0.5 to 69°C.

RESULTS AND DISCUSSION

Four factors which affect UV disinfection are soluble UV absorbing compounds, suspended solids, photoreactivation and equipment design. Soluble UV absorbing compounds simply absorb the UV light and lower the dosage of UV light received by the microorganisms. In addition to absorbing and scattering UV light suspended solids shield microorganisms from UV light. Exposure of UV irradiated microorganisms to sunlight can increase their numbers by as much as 10 fold or more (Whitby et al, 1984) and this is called photoreactivation. The equipment design can affect parameters such as the UV output of the lamps with changes in the temperature of the water and the intensity and retention time within the UV system.

The ability of a UV system to cope with changes in the water quality is also determined by the bacteriological standards which must be maintained. For chlorination a widely adopted bacterial standard is 200 fecal coliforms and 2500 total coliforms per 100 mL. In the United States the most common standard for UV disinfection is 200 fecal coliforms per 100 mL before photoreactivation. The one log increase in the number of coliforms (Whitby et al., 1984; Scheible and Bassell, 1981 and Bohm et al., 1982) after photoreactivation has not been addressed by the regulatory authorities in the United States. In Ontario, more stringent bacteriological limitations have been recommended for effluents irradiated with UV light. The suggested effluent design objectives are 500 total coliforms per 100 mL and/or 40 fecal coliforms per 100 mL as measured by the membrane filtration method. In Ontario, three WPCP have been specified with UV disinfection limits of 20 fecal coliforms per 100 mL before photoreactivation.

UV Light Absorption

Some effluents naturally contain a soluble UV absorbing compound or receive pulses of some UV absorbing material. To simulate these conditions the UV absorbing compound PHB was added to the effluent. An absorption spectrum of PHB confirmed that it only absorbed light below 294 nm with an absorption maximum at 250 nm. Figure 3 shows the effect of various concentrations of PHB on the UV transmission at 254 nm. Very little PHB was required to reduce the UV transmission and these concentrations had no effect on the enumeration of total and fecal coliforms.

The results of the bacteriological sampling at the various UV transmissions are shown in Figures 4 to 7 before and after photoreactivation of the coliforms. A regression analysis was used to plot the lines through the data and the equation for each line and its correlation coefficient are shown on the figures. The samples taken from in between the two matrices of UV lamps receive one half of the average dosage of UV light provided by the entire UV system. Therefore, the effect of every level of UV transmission was measured simultaneously at two dosage levels.

The geometric mean and standard deviation (SD) of the total and fecal coliforms per 100 mL in the influent were 67,286 (1 SD = 107,874) and 1533 (1 SD = 2330) respectively. The average flow through the UV units was 20.1 L/sec or 1.74 X 10^3 m^3/d. The chemical characteristics of the influent before the addition of PHB are shown in

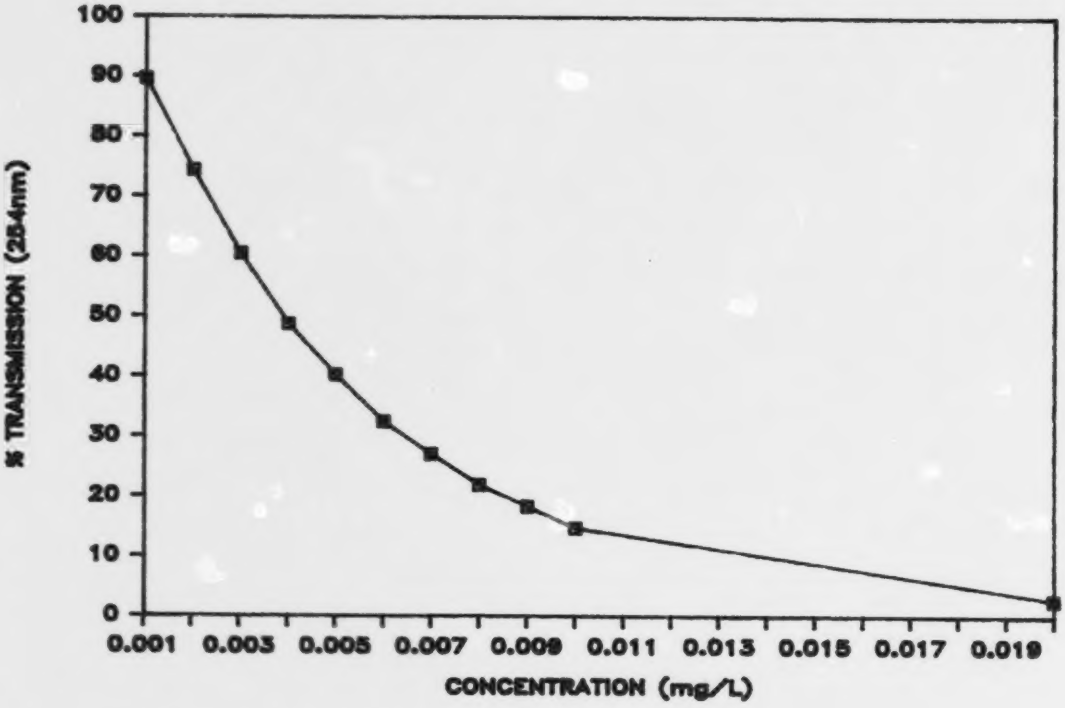

Figure 3: A curve of the concentration of parahydroxybenzoic acid versus the UV transmission at a wavelength of 254 nm.

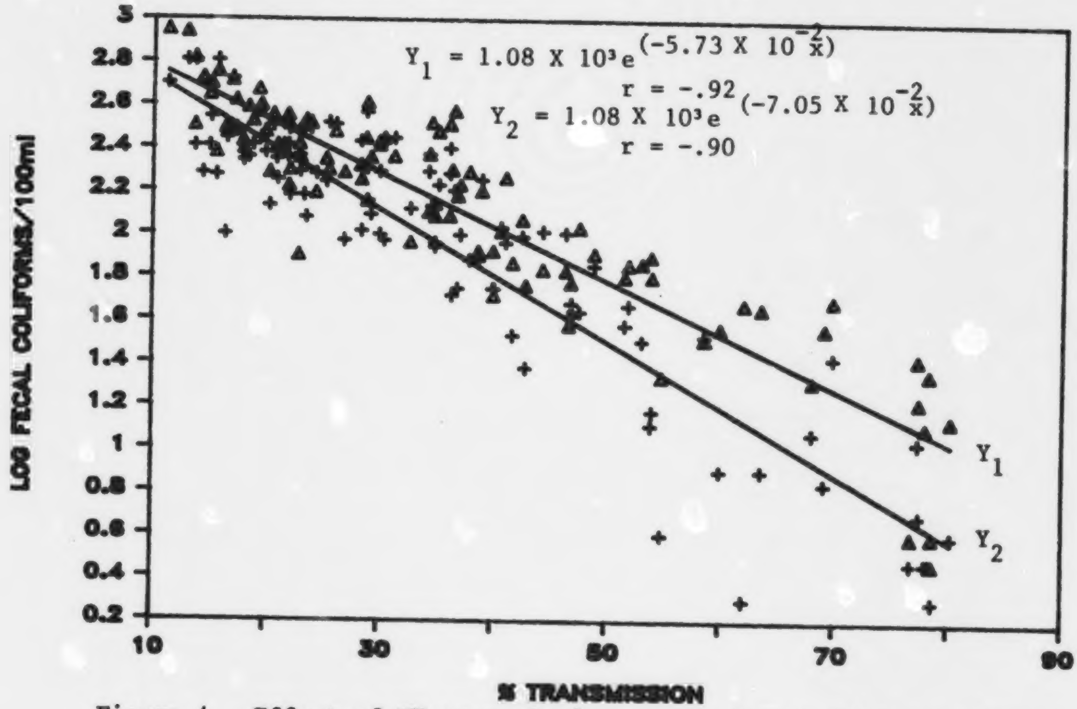

Figure 4. Effect of UV transmission on the fecal coliforms between the UV matrices before (+) and after (△) photoreactivation.

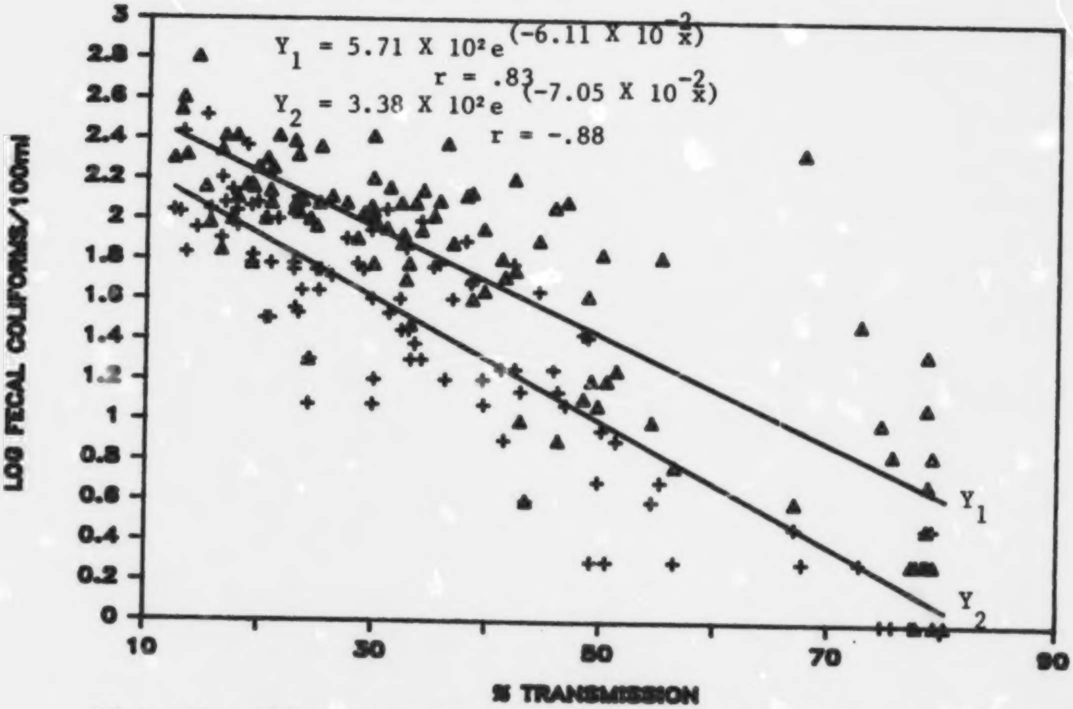

Figure 5. Effect of UV transmission on the fecal coliforms after the UV matrices before (+) and after (△) photoreactivation.

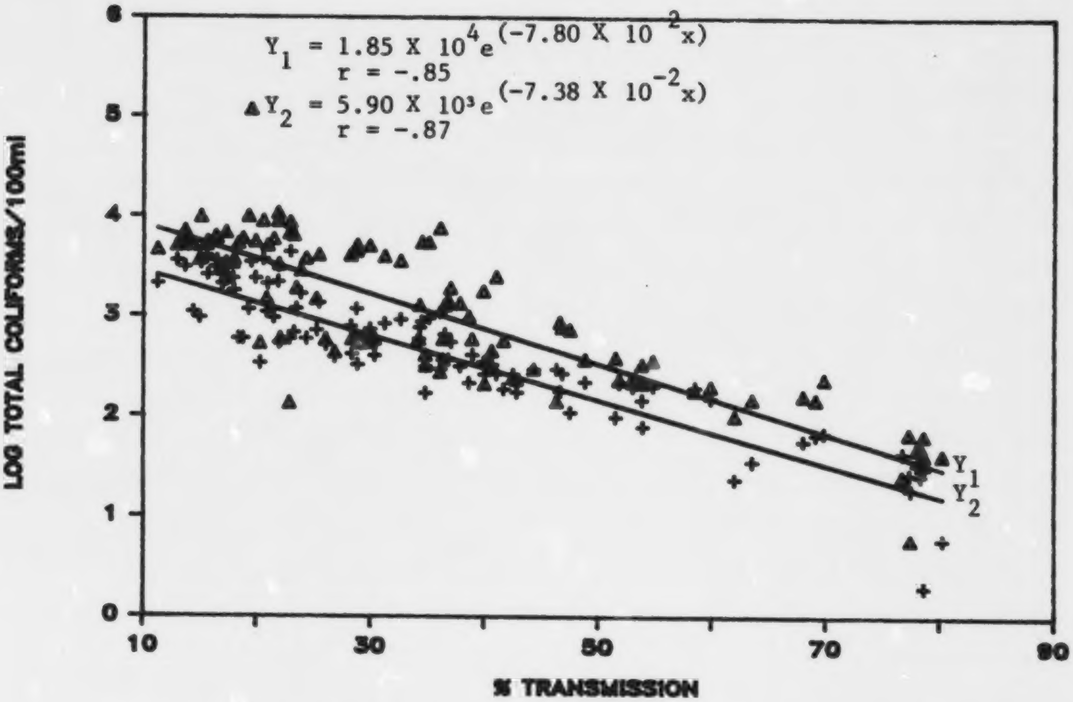

Figure 6. The effect of UV transmission on the total coliforms before (+) and after (Δ) photoreactivation.

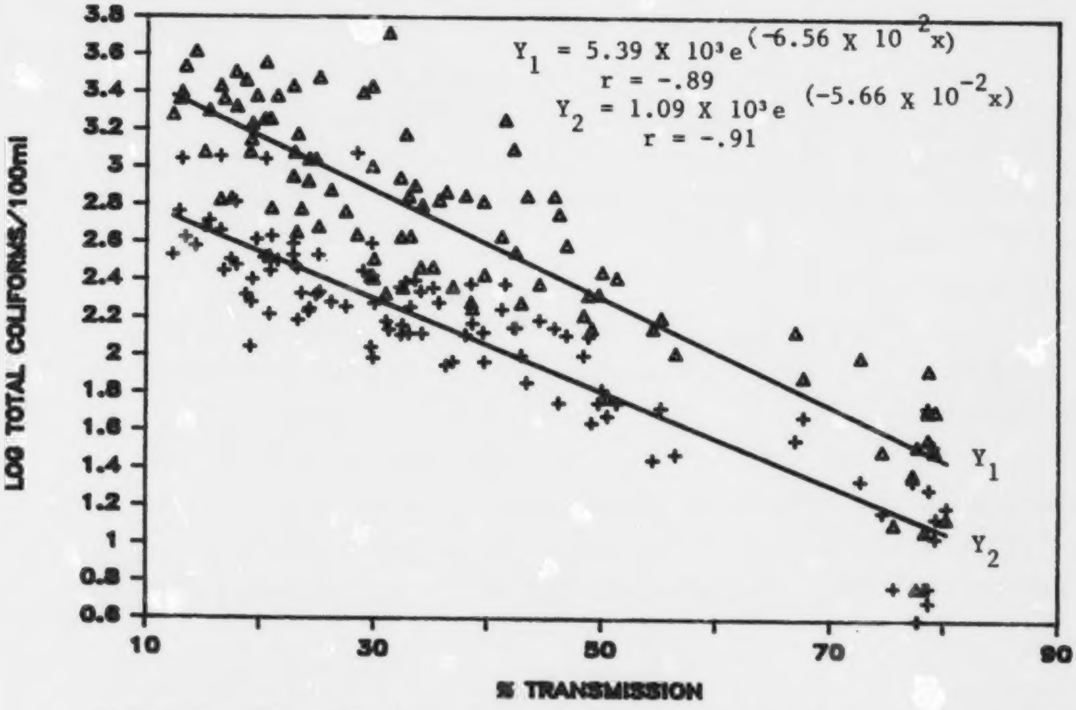

Figure 7. The effect of UV transmission on the total coliforms before (+) and after (Δ) photoreactivation.

Table 1. The average level of suspended solids throughout the study of the effect of UV transmission was 7.9 mg/l.

Tables 2 and 3 summarize the data from Figures 4 to 7 with respect to the suggested bacterial guidelines for total and fecal coliforms. Table 2 shows that in the United States where the fecal coliform limit is 200/100 mL before photoreactivation the UV system can disinfect an effluent which has a UV transmission of 7.5% when the UV lamps are new. The suggested guidelines for Ontario of 40 fecal coliforms per 100 mL increases the UV transmission to 30% which is 4 fold higher than that in the United States. The three WPCP in Ontario which have been specified with 20 fecal coliforms per 100 mL could only meet the requirements at 41% transmission which is 5.5 times higher than the 200 fecal coliform per 100 mL limit before photoreactivation. Table 3 shows that the total coliform limits of 2500 after photoreactivation or 500 before photoreactivation per 100 mL do not have as great an effect on the level of UV transmission which can be treated.

Doubling the UV dosage increases the UV transmission which can be treated by 1.4 to 3.2 times for the fecal coliforms and 2 to 2.3 times for the total coliforms depending upon the bacterial guidelines. The second matrix of UV lights is having a significant effect on the coliforms which have not been killed by the first array of UV lamps.

When total and fecal coliforms are exposed to sunlight after being UV irradiated a certain proportion will be photoreactivated. This results in an increase in the survival of the coliforms. From Figures 4 to 7 it can be seen that the coliforms photoreactivate at all of the levels of UV transmission. A two tailed paired Student's t-test showed that the photoreactivated and non-photoreactivated

Table 2. The lowest UV transmissions when the UV system can meet the suggested levels of fecal coliforms per 100 mL

	% UV Transmission			
Fecal Coliform Limit	200/100 mL	200/100 mL	40/100 mL	20/100 mL
Photoreactivation	No	Yes	No	No
Between UV Lamp Matrices	24	29	46	57
After UV System	7.5	17	30	41

Table 3. The lowest UV transmissions when the UV system can meet the suggested levels of total coliforms per 100 mL

Total Coliform Limit	2500/100 mL	500/100 mL
Photoreactivation	Yes	No
Between UV Lamp Matrices	24	33
After UV System	12	14

samples were significantly different at the $p = 10^{-6}$ level. Figures 8 to 11 show the ratio of photoreactivated to non-photoreactivated coliforms. There was a general increase in the number of photoreactivated fecal coliforms with increasing UV transmission whereas there was a slight decrease in the number of photoreactivated total coliforms. Unlike Whitby et al., 1984; Scheible and Bassel, 1981 and Bohm et al., 1982 a one log increase in the number of coliforms was not observed.

Suspended Solids

Suspended solids in wastewater can absorb and scatter UV light and they can also shield microorganisms from the UV light.

The effect of suspended solids on the absorption and scattering of UV light is shown in Figure 12. The effects of absorption and scattering were not separated although this is possible (Qualls et al., 1983). At the highest concentration of suspended solids which was tested the UV transmission was approximately 15%. Light at a wavelength of 660 nm is scattered by the suspended solids and not absorbed. Figure 13 shows how light scattering can affect the transmission of light. UV light which is scattered is still able to kill microorganisms. Therefore UV transmission as commonly measured is a conservative estimate of the actual UV absorbance when suspended particles are present.

The results of the bacterial concentrations before and after photoreactivation at the various levels of suspended solids are shown in Figures 14 to 17. A regression analysis was used to plot the lines through the data and the equation for each line and its correlation

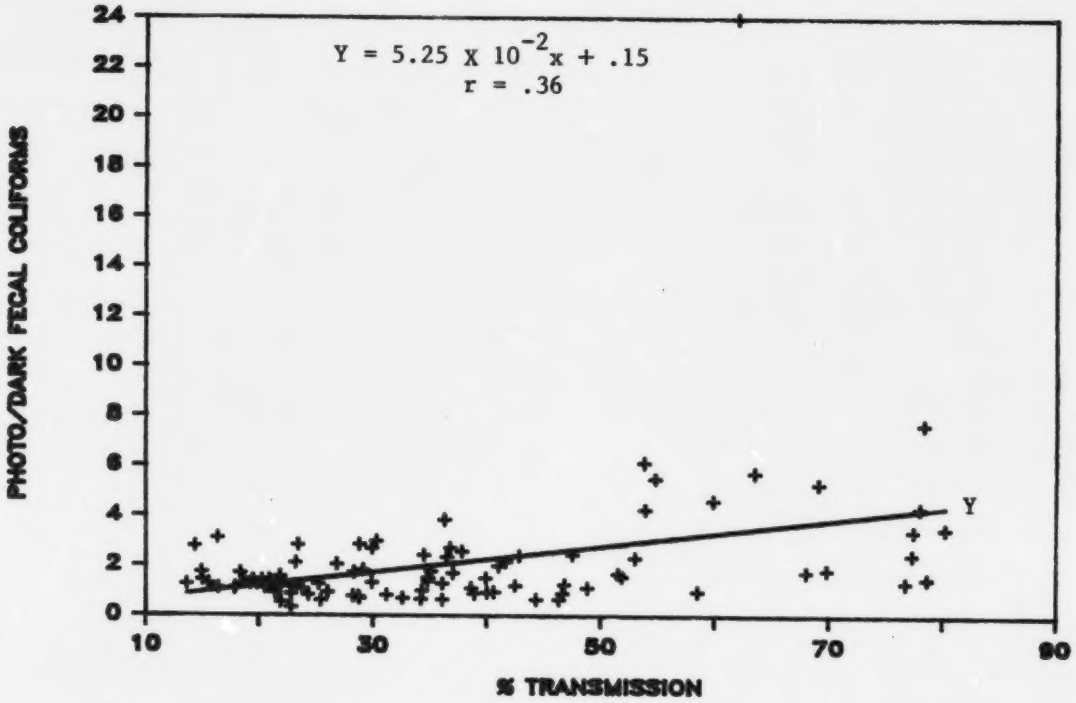

Figure 8. Ratio of the photoreactivated and non-photoreactivated fecal coliforms between the UV matrices.

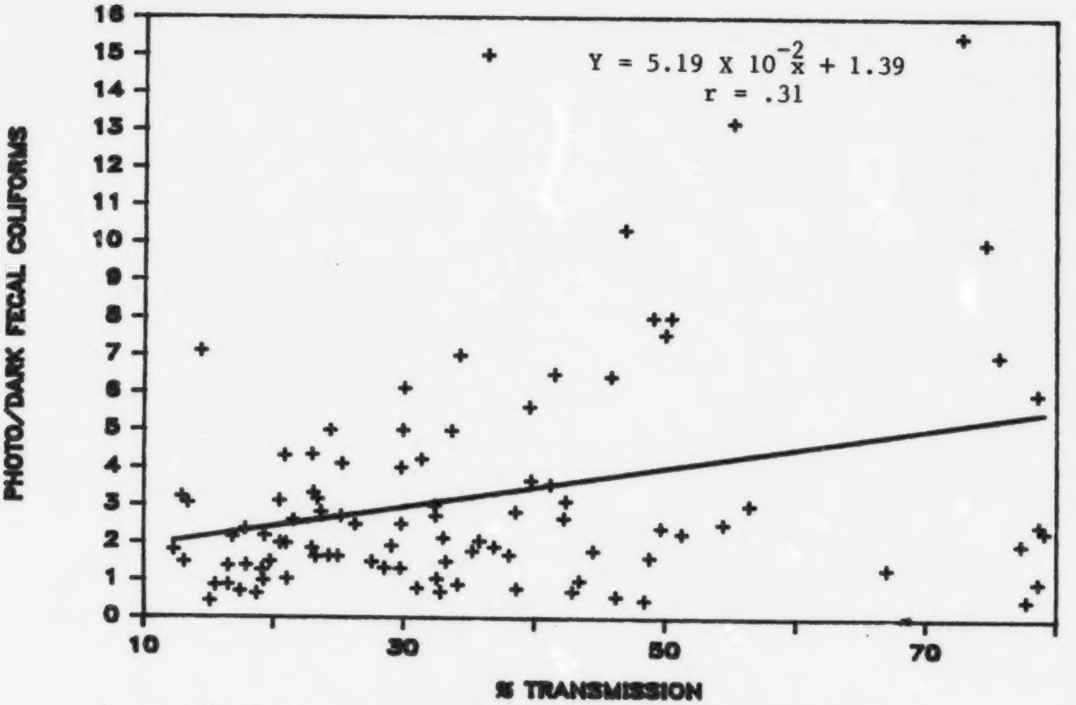

Figure 9. Ratio of the photoreactivated and non-photoreactivated fecal coliforms after the UV matrices.

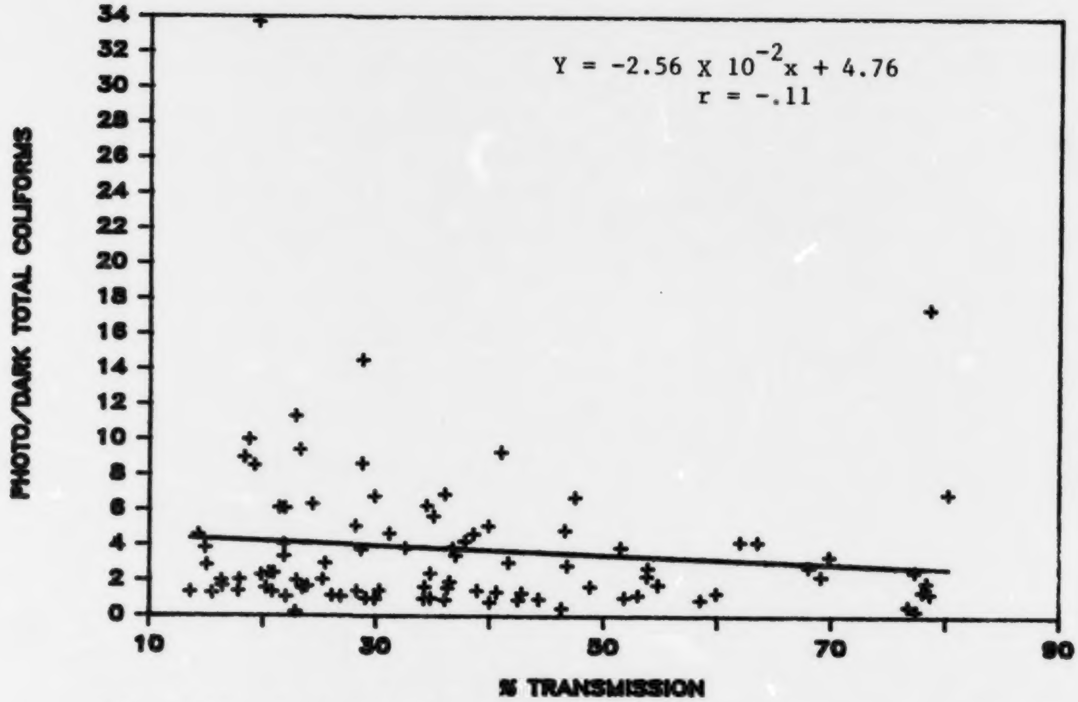

Figure 10. Ratio of photoreactivated to non-photoreactivated total coliforms between the UV matrices.

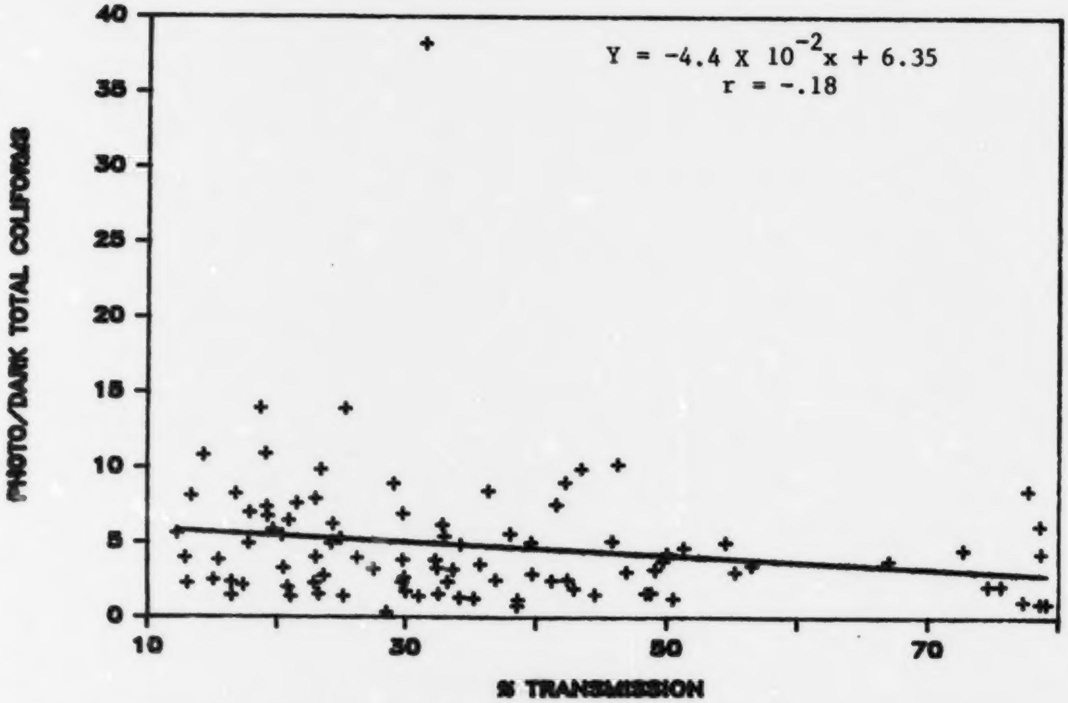

Figure 11. Ratio of photoreactivated to non-photoreactivated total coliforms after the UV matrices.

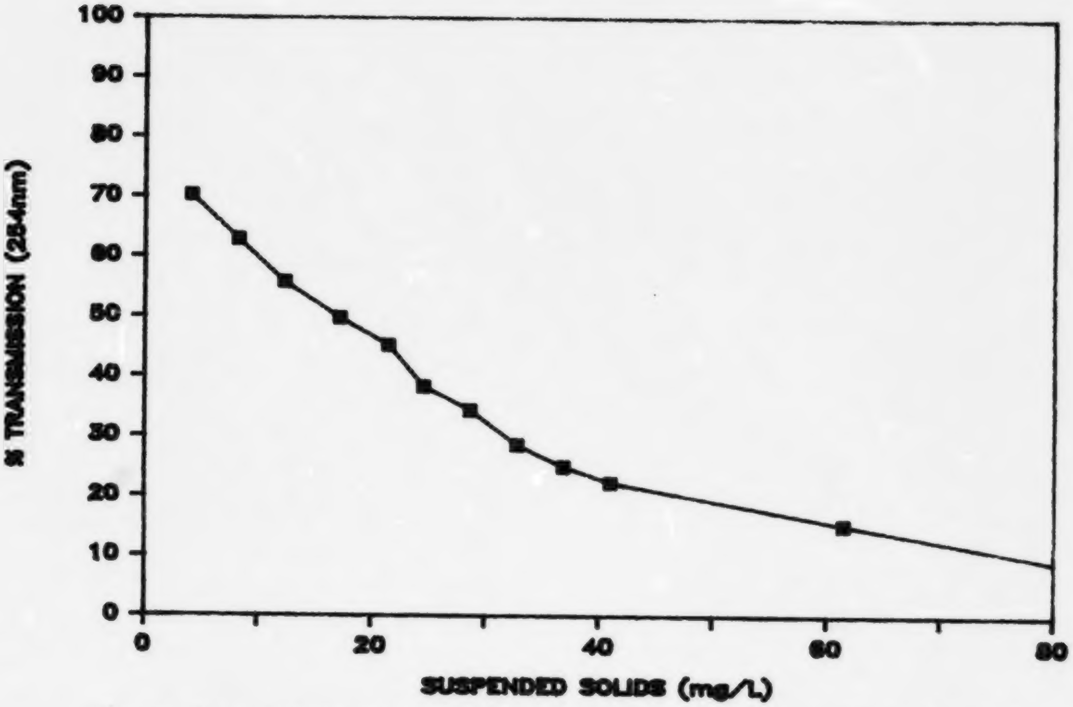

Figure 12. Effect of suspended solids on the UV transmission of deionized water.

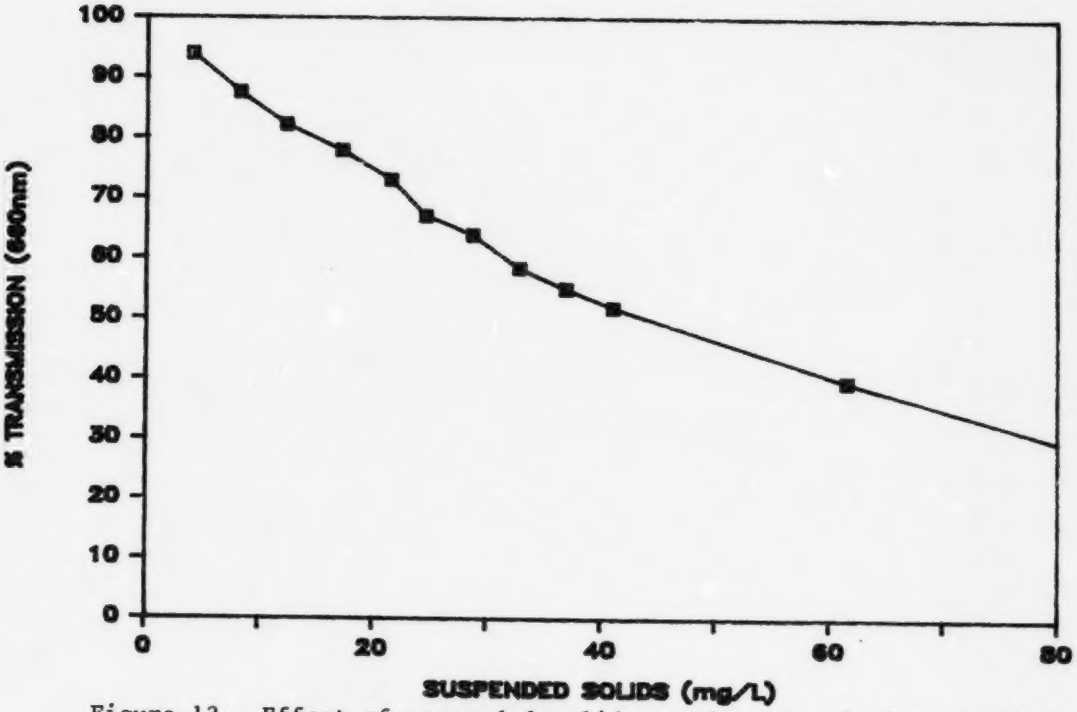

Figure 13. Effect of suspended solids on the transmission of light at a wavelength of 660 nm.

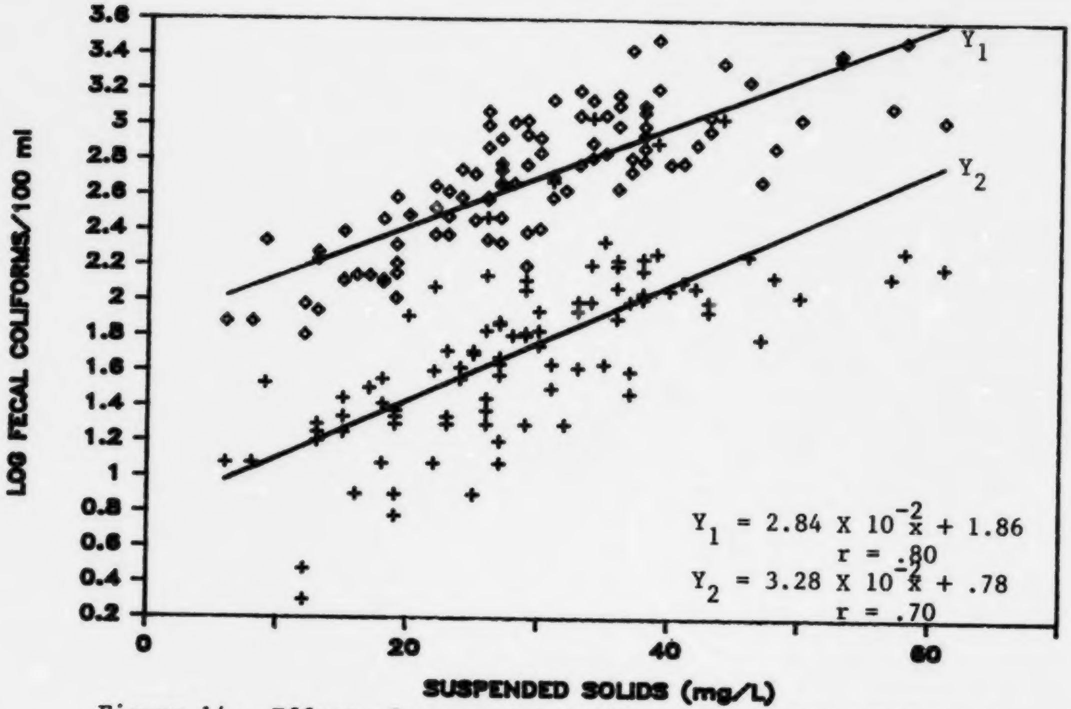

Figure 14. Effect of suspended solids on the fecal coliforms between the UV matrices before (+) and after (◇) photoreactivation.

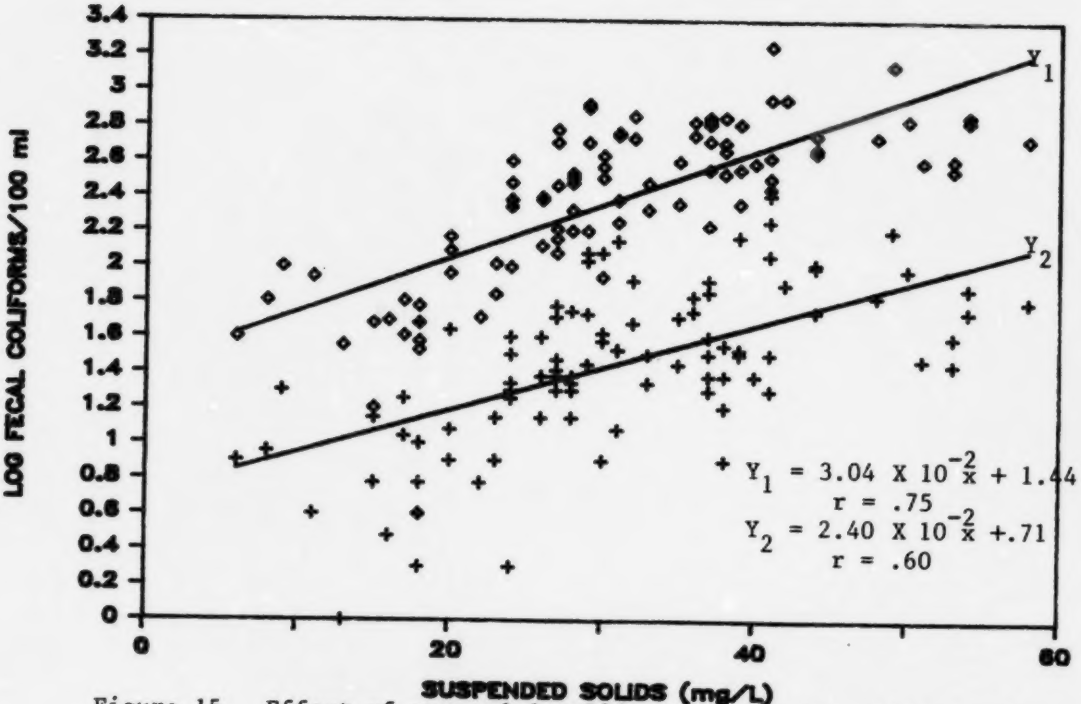

Figure 15. Effect of suspended solids on the fecal coliforms after the UV matrices before (+) and after (◇) photoreactivation.

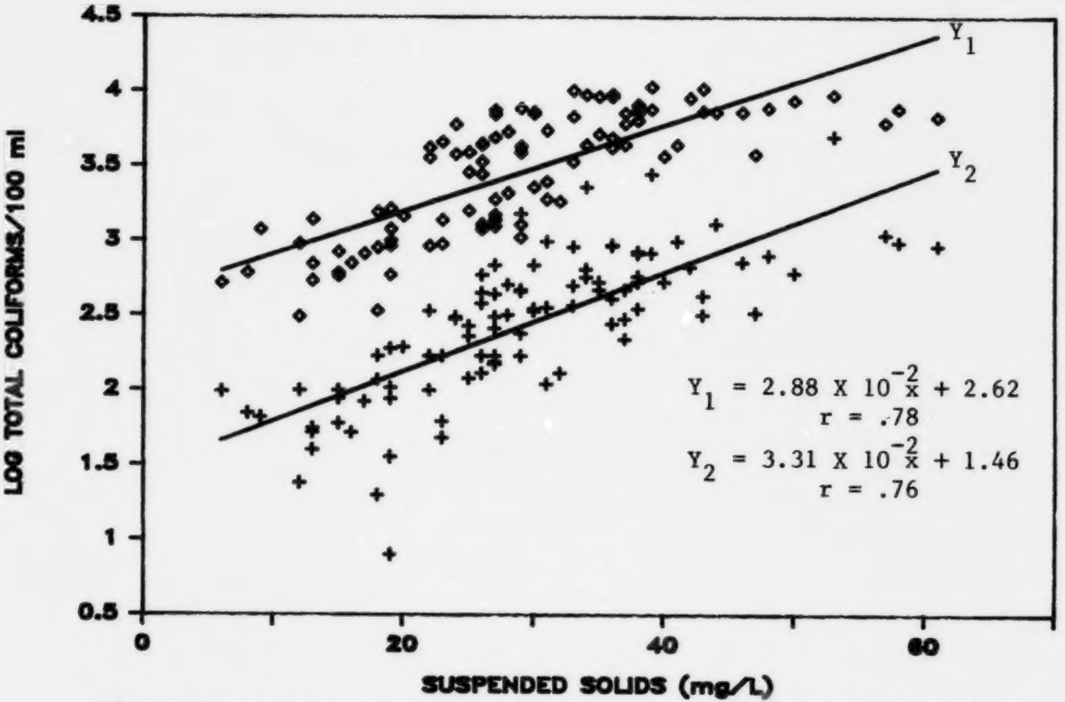

Figure 16. Effect of suspended solids on the total coliforms between the UV matrices before (+) and after (◇) photoreactivation.

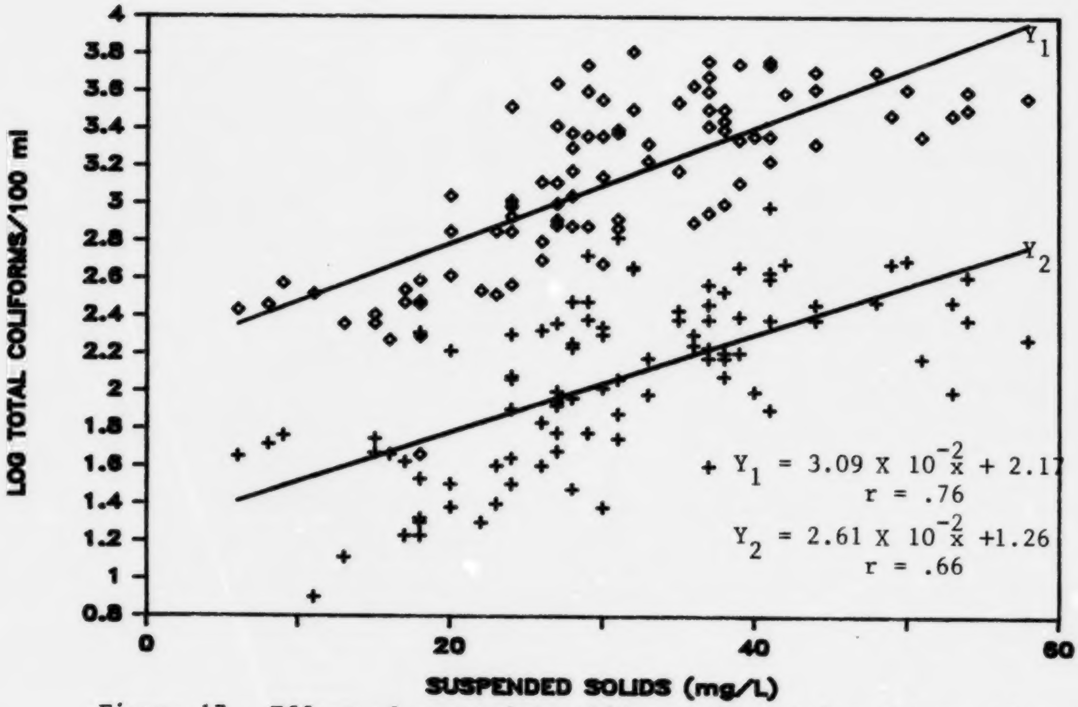

Figure 17. Effect of suspended solids on the total coliforms after the UV matrices before (+) and after (◇) photoreactivation.

coefficient are shown on the figures. The average flow through the UV units was 30.6 L/sec or 2.65 X 10^3 m^3/d.

Tables 4 and 5 summarize the data from Figures 14 to 17 with respect to the suggested bacterial guidelines for fecal and total coliforms. Table 4 shows that in the United States where the fecal coliform limit is 200/100 mL before photoreactivation the UV system can disinfect an effluent which has 65 mg/L of suspended solids when the UV lamps are new. The suggested guidelines for Ontario of 40 fecal coliforms per 100 mL decreases the suspended solids to 37 mg/L which is 43% less solids than the guidelines for the United States. The three WPCP in Ontario which have been specified with 20 fecal coliforms per 100 mL could only meet the requirements at 25 mg/l of suspended solids which is 61% less than the limit of 200 fecal coliforms per 100 mL before photoreactivation. As shown in Table 5 the suggested guidelines for total coliforms of 500 per 100 mL allowes more solids to be treated than a limited of 2500 total coliforms per 100 mL after photoreactivation. After photoreactivation the fecal coliform level of 200/100 mL could be met at a solids levels of 28 mg/L.

Doubling the UV dosage increases the levels of suspended solids which can be treated by 1.4 to 2 times for the fecal coliforms and approximately 1.5 times for the total coliforms depending upon the bacterial guidelines. Therefore, the second array of UV lamps is having a significant impact on UV disinfection.

Figures 14 to 17 show that the coliforms increased in numbers after they were exposed to sunlight and allowed to photoreactivate. A two tailed paired Students t-test showed that the photoreactivated and non-photoreactivated samples were significantly different at the $p = 10^{-6}$ level. Figures 18 to 21 show the ratio of the photoreactivated to

Table 4. The highest level of suspended solids (mg/L) when the UV system can meet the suggested levels of fecal coliforms per 100 mL

		SUSPENDED SOLIDS (mg/L)		
Fecal Coliform Limit	200/100 mL	200/100 mL	40/100 mL	20/100 mL
Photoreactivation	No	Yes	No	No
Between UV Lamp Matrices	36	14	25.5	17
After UV System	65	28	37	25

Table 5. The highest level of suspended solids (mg/L) when the UV system can meet the suggested levels of total coliforms per 100 mL.

	SUSPENDED SOLIDS (mg/L)	
Total Coliform Limit	2500/100 mL	500/100 mL
Photoreactivation	Yes	No
Between UV Lamp Matrices	26	37
After UV System	40	53

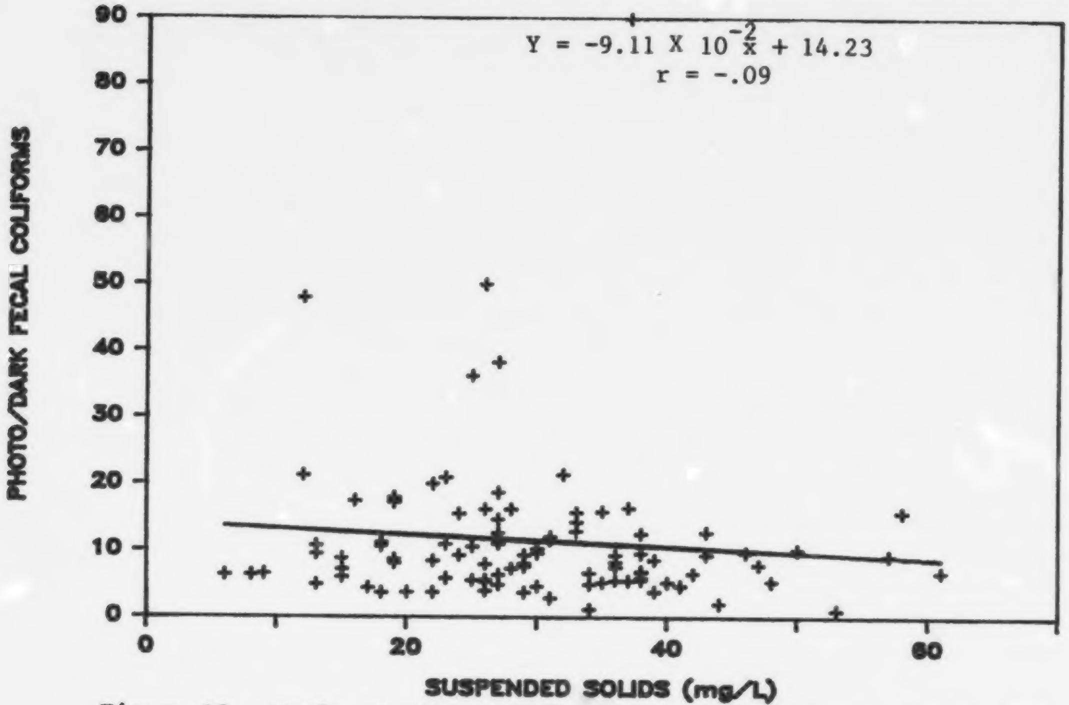

Figure 18. Ratio of photoreactivated to non-photoreactivated fecal coliforms between the UV matrices.

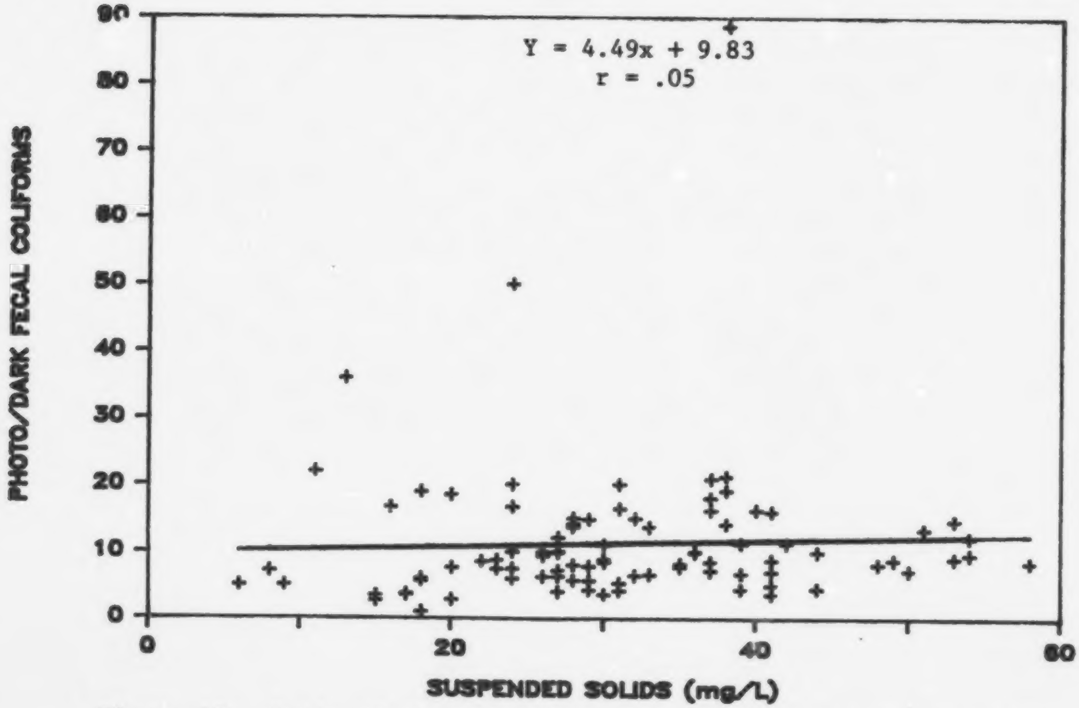

Figure 19. Ratio of photoreactivated to non-photoreactivated fecal coliforms after the UV matrices.

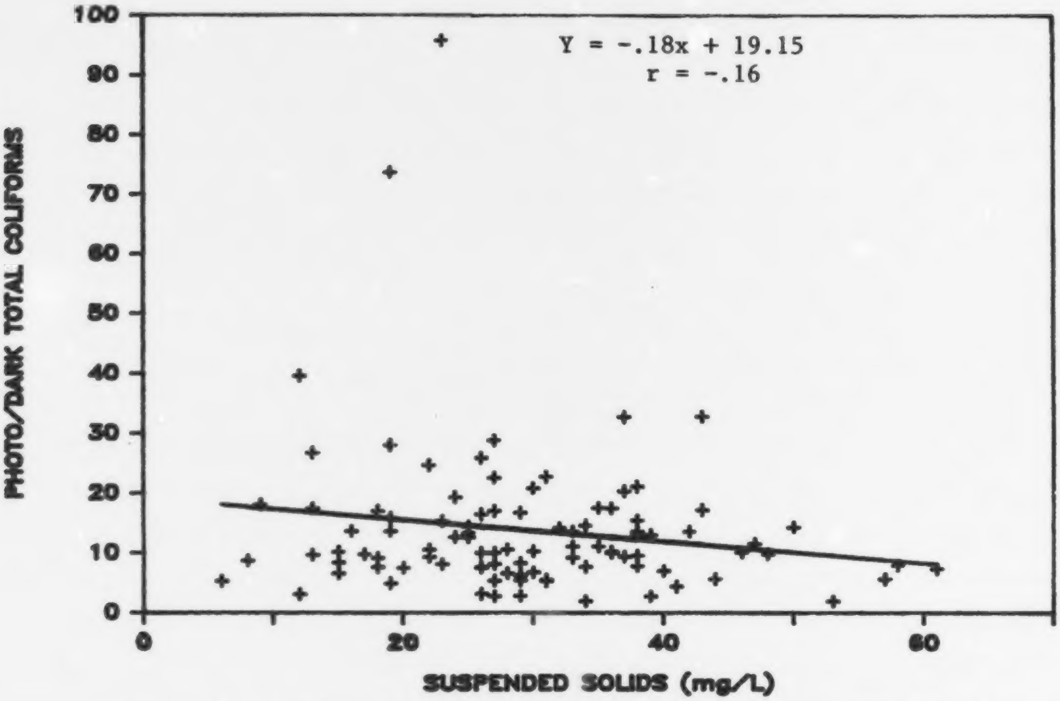

Figure 20. Ratio of photoreactivated to non-photoreactivated total coliforms between the UV matrices.

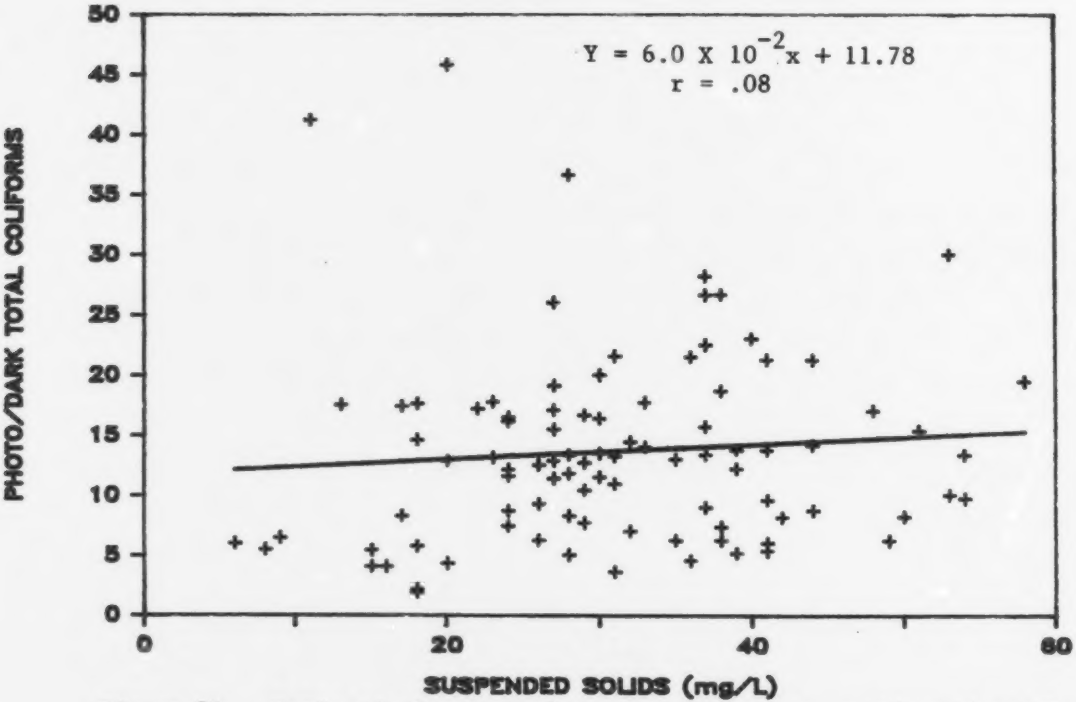

Figure 21. Ratio of photoreactivated to non-photoreactivated total coliforms after the UV matrices.

non-photoreactivated coliforms. The degree of photoreactivation was almost constant over the range of suspended solids. The increase in coliform level was approximately one log. This is much higher than that observed during the study of UV transmission but it is similar to that observed by other researchers (Whitby *et al.*, 1984; Scheible and Bassell, 1981 and Bohm *et al.*, 1982).

UV Lamp Output Versus Temperature

The lamp and quartz sleeve which are used in the UV system can affect the UV output of the lamps. Figure 22 describes the effect of water temperature on the relative output of the UV lamp and quartz sleeve used in this UV system. Temperatures from 4°C to 30°C have less than a 10% effect on the output of the lamps. This range of temperatures would cover most situations which occur in North America.

UV Lamp Output Versus Usage

The longer a UV lamp can maintain its output and still meet the bacterial guidelines is important from an economic standpoint. The UV lamps account for the majority of the maintenance costs. Figure 23 shows the effect of time on the percentage output of the UV lamps in the system at Tillsonburg. These lamps have a warranty of 7500 hours. After 28,000 hours the UV system was still able to meet the bacterial guideline of 2500 total coliforms per 100 mL and 200 fecal coliforms per 100 mL after photoreactivation. Only 2 lamps out of 80 would not burn after 28,392 hours of continuous use.

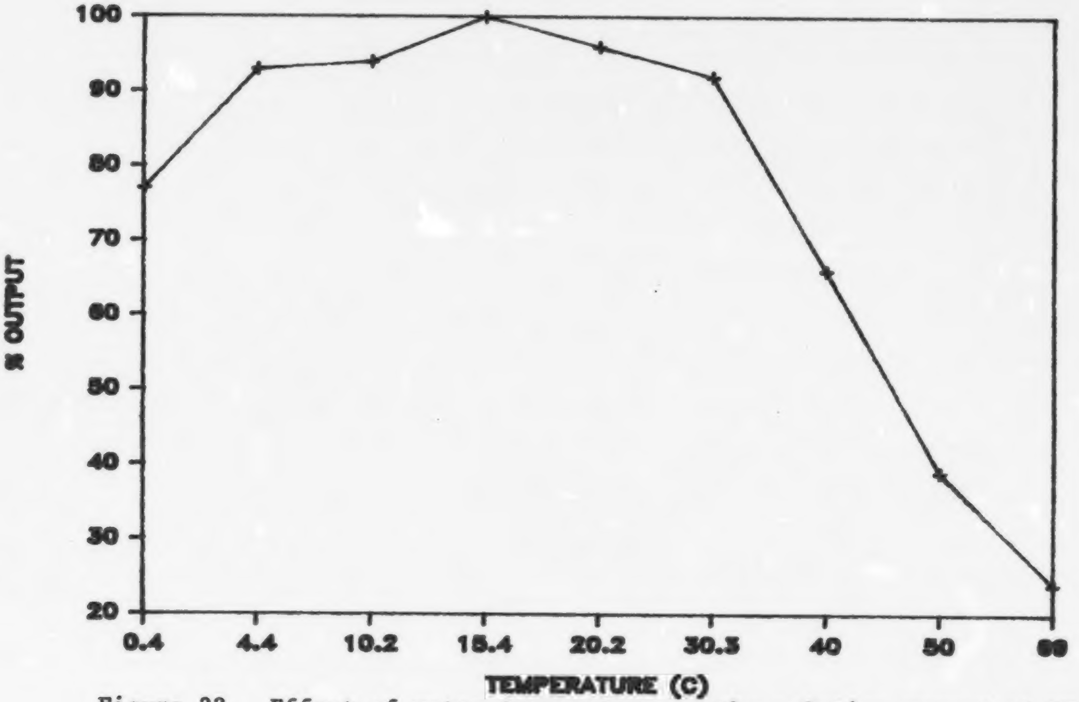

Figure 22. Effect of water temperature on the relative output of UV light in the UV system.

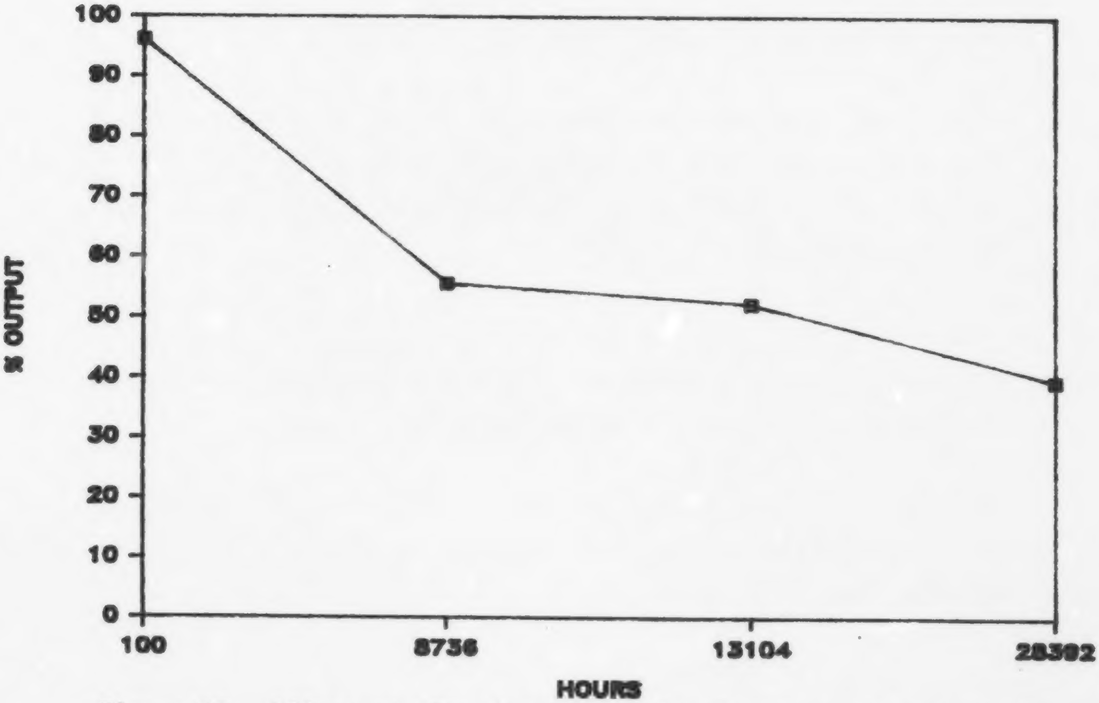

Figure 23. Effect of time (hours) on the UV output (watts) of the lamps in the UV system.

CONCLUSIONS

1. Suspended solids have a greater effect on UV disinfection than UV transmission. Clumps of microorganisms or other material may provide more protection for bacteria than UV absorbing compounds.

2. The suggested guidelines for the total and fecal coliforms are attained at different levels of UV transmission and suspended solids. This differential will have to be addressed in terms of the survival and possible photoreactivation of pathogenic bacteria in order that a meaningful standard be adopted.

3. Photoreactivation occurs at all the levels of UV transmission and suspended solids which were tested. Photoreactivation must be taken into account when bcterial standards are developed.

4. The difference between the degree of photoreactivation during the study of UV transmission and suspended solids should be examined.

5. The temperature of wastewaters in North American does not appear to have a significant effect on the UV output of the lamp and quartz sheath combination which is used in this UV system.

6. The effective operational period of the UV lamps utilized in this study of nearly 3 years is far in excess of the predicted manufacturer's value.

7. A more detailed study of the UV output of the lamps will determine the actual intensities and dosages within the UV system.

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THE TECHNICAL AND ECONOMIC FEASIBILITY OF RETROFITTING EXISTING MUNICIPAL TREATMENT PLANTS IN CANADA FOR BIOLOGICAL PHOSPHORUS REMOVAL

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Key words: Sewage Treatment, Phosphorus Removal, Activated Sludge.

ABSTRACT

The technical and economic feasibility of retrofitting existing wastewater treatment plants in Canada for biological phosphorus removal was evaluated, with the objective of establishing the type and size of facilities which would be most amenable to implementation of these technologies. The cost analyses were based on model treatment plants having idealized configurations representative of standard design practices. Effluent total phosphorus limits of 1.0 mg/l and 0.3 mg/l were imposed on the processes for the purposes of the cost comparison.

The technical review demonstrated that the four biological phosphorus removal (EBPR) processes evaluated - Bardenpho, UCT, A/O and Phostrip - were capable of producing a final effluent containing between 1.0 and 2.0 mg/l total phosphorus. To consistently achieve effluent phosphorus limits of less than 1.0 mg/l, EBPR processes require some combination of effluent filtration and/or supplemental chemical addition. Further, it was found that ideally, EBPR and chemical phosphorus precipitation processes should be considered to be complimentary processes which should be applied simultaneously to optimize performance and minimize the costs of achieving phosphorus control.

EBPR processes typically involved higher capital investment than chemical precipitation in retrofit situations. However, in conventional activated sludge plant retrofits at a hydraulic capacity of 36.4 Ml/d, the annual O & M costs of all EBPR options with the exception of Phostrip were lower than the O & M costs of chemical precipitation. Financing the higher capital expenditures associated with EBPR processes resulted in generally higher total annual costs for these processes than for chemical precipitation. Only A/O was more cost-effective than chemical precipitation based on total annual costs in any of the retrofit situations evaluated.

In new facilities, conventional activated sludge plants incorporating simultaneous chemical precipitation for phosphorus removal were more cost-effective based on total annual costs than all EBPR processes except A/O. On the basis of annual O & M costs, A/O was generally more cost-effective than the conventional plant, and when a 0.3 mg/l effluent total phosphorus limit was imposed, all EBPR processes except Phostrip had lower annual O & M costs than the conventional plant at a hydraulic flow of 13.6 Ml/d or more.

Conventional activated sludge plants of hydraulic capacity in excess of approximately 14 Ml/d were found to be most amenable to EBPR process retrofits based on the economic evaluation. However, factors such as the existing effluent nutrient limits imposed on WPCPs, the design of existing facilities and the characteristics of wastewaters in Canada combine to limit the number of candidates for retrofit of EBPR technologies. Circumstances which would lead to more widespread implementation of EBPR processes include the imposition of more stringent phosphorus and nitrogen removal requirements, major increases in chemical costs and the development of a greater level of confidence in the performance of EBPR processes.

ABSTRACT

An economic analysis was conducted to compare the cost effectiveness of four biological phosphorus removal processes with the traditional chemical precipitation approach to phosphorus removal in retrofit situations. It was found that the biological processes typically involved higher capital investments, but annual O&M costs were lower than those for chemical precipitation in conventional activated sludge plant retrofits at a hydraulic capacity of 36,400 m^3/d. Factors such as the effluent phosphorus and nitrogen limits imposed on the facility, the wastewater characteristics, the type, size and configuration of the existing plant, sludge management practices and degree of confidence in the performance of the biological alternatives impact on process selection.

TECHNICAL AND ECONOMIC FEASIBILITY OF RETROFITTING EXISTING MUNICIPAL WASTEWATER TREATMENT PLANTS IN CANADA FOR BIOLOGICAL PHOSPHORUS REMOVAL

S.G. Nutt, N.W. Schmidtke and B.H. Paepcke

INTRODUCTION

Since phosphorus was recognized as a major contributor to the eutrophication of receiving waters, regulatory agencies have placed increasingly stringent limits on the concentration of phosphorus in discharges from municipal wastewater treatment facilities. The conventional approach used for phosphorus removal has been chemical precipitation by the addition of a metal salt such as alum, ferric chloride or lime. Experience in Ontario has demonstrated that chemical phosphorus precipitation is a simple, effective technology capable of consistently achieving effluent total phosphorus levels of less than 1 mg/L. At the same time, this experience has shown that the costs of chemical precipitation increase dramatically when more stringent limits are placed on the total phosphorus concentration in the process effluent.

Concurrent with the implementation of chemical phosphorus removal technologies, researchers began to identify that, in some situations, activated sludge micro-organisms were capable of achieving higher degrees of phosphorus removal than considered typical. Proper sequencing of anaerobic, anoxic and aerobic environments resulted in enhanced biological phosphorus removal (EBPR) and the EBPR concept has become embodied in several process flowsheets. Lower O&M costs, due to the elimination of chemical addition requirements and the reduction in sludge generation rates compared to conventional chemical phosphorus removal systems, have been touted as a major advantage of the EBPR process options.

In Canada, most communities are already served by a wastewater treatment facility of some type. Thus, in many cases, the implementation of biological phosphorus removal processes will involve a retrofit to an existing facility. This investigation addressed the technical and economic feasibility of retrofitting existing Canadian municipal wastewater treatment plants for biological phosphorus removal. Cost comparisons between a number of biological process alternatives and chemical precipitation technology were made. The study was not limited to a single specific plant, but was conducted in a broader context so that those conditions under which either chemical or biological phosphorus removal was more cost-effective could be identified.

SCOPE OF WORK

In order to streamline the investigation and reduce the number of retrofit situations requiring cost analysis to a manageable level, the scope of work was limited to the following situations:

(i) Three types of plants were considered for retrofitting to biological phosphorus removal processes; primary plants, conventional activated sludge plants and extended aeration plants. Each plant type was evaluated at three flows representative of the typical sizes of these types of plants in Ontario. The plant sizes selected are summarized in Table 1.

(ii) The biological nutrient control technologies evaluated included the three commercially available processes presently used in North America - Bardenpho, Phostrip, and A/O - as well as the developmental UCT process.

(iii) Phosphorus precipitation with ferric chloride was used for the purposes of developing comparative costs for the chemical precipitation process.

(iv) Two total phosphorus discharge limits were imposed on the effluents from the treatment facilities - 1.0 mg/L and 0.3 mg/L TP. As it was not considered technically feasible to achieve the lower limit (0.3 mg/L) by chemical addition to a primary plant due to the high suspended solids concentrations in primary effluents, this cost analysis was done only to a limit of 1.0 mg/L TP.

(iv) The raw wastewater characteristics were assumed to be:

COD = 250 mg/L
TKN = 25 mg/L
Alkalinity = 240 mg/L
Total Phosphorus = 5 mg/L

METHODOLOGY

Model Plant Designs

A standardized design for each type of plant (primary, conventional activated sludge and extended aeration) was developed, based on Ontario Ministry of the Environment design guidelines(1). These model plants formed the basis for the process retrofits to achieve phosphorus control. Details of the design criteria for each model plant have been presented elsewhere(2).

The model primary plant consisted of headworks (bar screen, aerated grit chamber, comminutor and Parshall flume), primary clarifier including raw sludge pumping station, single-stage anaerobic digester and chlorine contact chamber. The model conventional activated sludge plant incorporated the same headworks as the model primary plant, primary clarifiers with raw sludge pumping station, aeration basins with mechanical surface aerators, secondary clarifiers with return sludge pumping station, two-stage (primary and secondary) anaerobic digestion and chlorine contact chamber.

The layout of the model extended aeration plant deviated somewhat from standard design practices. In the smaller size ranges (less than 2000 m^3/d), packaged treatment plant configurations are commonly used. These small package treatment plants, which typically incorporate common-wall, steel-tank construction for aeration tanks, clarifier and sludge holding tanks, are not well-suited for retrofitting to biological phosphorus removal processes. Therefore, the extended aeration plants were designed as standard mechanical plants with separate components rather than as packaged plants for the purposes of this cost assessment. Process components included the headworks as in the other model plants, the aeration basin equipped with mechanical aerators, secondary clarifier with return sludge pumping station, an aerated sludge holding tank and the chlorine contact chamber.

Design of Chemical Phosphorus Removal Processes

To establish a basis for cost comparison, the model primary, conventional activated sludge and extended aeration plants were retrofitted for chemical precipitation of phosphorus.

The retrofit designs of the secondary plants (conventional activated sludge and extended aeration) were based on simultaneous precipitation of phosphorus by the addition of ferric chloride to the aeration tank. Chemical dosages of 8 mg Fe/L to achieve an effluent total phosphorus limit of 1.0 mg/L and 14 mg Fe/L to achieve an effluent total phosphorus limit of 0.3 mg/L were selected(3). A final effluent granular media filter was included in the flow scheme to achieve the lower total phosphorus limit. In the case of the primary plant, retrofit costs to achieve the lower phosphorus limit (0.3 mg/L) were not developed.

In the case of the primary plant, a 40 percent increase in sludge generation was assumed after implementation of chemical phosphorus removal to the 1.0 mg/L discharge limit(4). A 26 percent increase in sludge generation was assumed for the secondary plants (conventional activated sludge and extended aeration) retrofitted for chemical phosphorus removal to the 1.0 mg/L limit(4). An overall increase of 42 percent in sludge generation was assumed in the secondary plants retrofitted to achieve the lower (0.3 mg/L) effluent phosphorus limit.

Design of Biological Phosphorus Removal Processes

The designs of the biological nutrient control processes were based on a thorough review of present design practices for pilot scale, demonstration scale and full scale examples of these technologies. The Bardenpho system was designed as a five-stage process for maximum biological nutrient control. The UCT system was designed as a three-stage system. A/O was designed as a two-stage system, without biological nitrogen control. These designs were intended to cover the entire range of nutrient control (nitrogen and phosphorus) achievable with the EBPR processes. In the case of Phostrip, the mainstream biological process did not provide for biological nitrification. Schematic flowsheets of each EBPR process are presented in Figure 1. For the totally biological options (Bardenpho, A/O and UCT), the primary clarifiers in the model plants were by-passed to maximize the organic content of the raw wastewater input to the anaerobic basins.

The design of the Bardenpho, A/O and UCT systems to achieve the higher effluent total phosphorus limit (1.0 mg/L) followed two approaches; EBPR plus effluent polishing by dual media filtration and EBPR plus supplemental ferric chloride addition to reduce the soluble orthophosphorus concentration in the effluent. The designs of these processes to achieve the lower effluent total phosphorus limit (0.3 mg/L) incorporated both dual media filtration and supplemental ferric chloride addition. The ferric chloride dosage rate was 6 mg Fe/L.

In the case of the Phostrip designs, the plants designed to achieve 1.0 mg/L effluent total phosphorus incorporated only the Phostrip process retrofit. Designs to achieve the lower effluent limit incorporated effluent dual media filtration. The Phostrip process was designed with a recycle stripping tank, with phosphorus precipitation by lime addition in a dedicated reactor-clarifier.

The EBPR process retrofits were designed to maximize the use of the existing equipment to the greatest extent possible. For example, in the primary plant retrofit situations, the flow scheme was modified to allow the model plant primary clarifier to be utilized as the secondary clarifier in the retrofitted plant. Existing aeration tankage was reused as much as possible, but compartmentalization was incorporated by the addition of concrete partitions and sluice gates. To provide feasibility in the various reaction zones (anaerobic, anoxic and aerobic), submerged turbine aerators were designed into the retrofitted EBPR processes. Mixing energy in the anoxic and anaerobic reactors was 10 W/m^3. Blower facilities provided the additional oxygen transfer capability required to meet the carbonaceous (and nitrogenous) oxygen demand.

Phostrip plant designs incorporated a bag storage and feeder system for plants with a design flow of less than 4500 m^3/d. For larger plants, a bulk lime silo storage system was incorporated. The lime dosage to the stripper, at 240 mg $Ca(OH)_2/L$, and solids production from the lime precipitation process, at 0.5 kg dry solids per m^3 stripper supernatant, were based on stoichiometric calculations.

Costing Methodology

The capital and operating costs for each model plant were developed using CAPDET, which was developed by the United States Army Corp of Engineers on behalf of the U.S. EPA(5). This computer model estimates total capital costs, and operation and maintenance (O&M) costs based on process design specifications, wastewater and effluent characteristics and unit cost data which are provided as user input to the model. It has been shown that CAPDET is capable of estimating construction costs to within ± 20 percent of actual costs and O&M costs to within ± 30 percent for Canadian situations provided that care is taken to ensure that process design details and internal recycle streams are maintained within realistic ranges(6).

A list of process equipment or accessories required to retrofit each type of model plant to chemical or biological phosphorus removal was developed. This accessory list included such hardware as pumps, piping, tankage, blowers, mixers, granular media filters and lime feed equipment. Capital and O&M cost curves were developed for each type of equipment for a range of flows up to 40,000 m^3/d. These costs curves were based on equipment vendors' information and on cost data included in the CAPDET model.

The costs of retrofitting the model plants to achieve phosphorus removal, by either biological or chemical means, were developed by selecting the required retrofit hardware and determining the costs (capital and operating) of this hardware from the pertinent cost curve at the required flow. These retrofit equipment costs were then added to the model plant costs developed from the CAPDET model. Wherever appropriate, cost credits for existing or redundant equipment were assigned to the retrofit. For example, in situations where the primary clarifier was by-passed, an O&M cost credit was assigned equivalent to the O&M cost associated with the operation of the primary clarifier.

After assignment of costs of all retrofit hardware and consideration of all pertinent cost credits, capital costs, O&M costs and total annual costs were calculated for each retrofit situation. O&M costs and total annual costs were expressed relative to the mass of phosphorus removed ($ per kg total phosphorus removed). The calculated costs represent the additional costs associated with implementation of phosphorus removal and not the total costs of plant construction and operation.

RESULTS OF COST ANALYSES

Incremental total annual costs, expressed on a '$ per kg total phosphorus removed' basis, are presented. Detailed breakdowns of the incremental capital costs, incremental annual O&M costs and incremental total annual costs are available elsewhere(2). Costs are expressed in 1985 Canadian dollars.

Bardenpho Retrofit Costs

The costs of retrofitting the model plants to achieve phosphorus control by the Bardenpho process are compared to the costs of achieving similar control by chemical precipitation technology in Figure 2.

The cost data demonstrate the cost advantage associated with achieving the 1.0 mg/L effluent total phosphorus limit by chemical supplementation as compared to the costs of achieving this limit by effluent filtration. However, in all cases, chemical precipitation technology was more cost-effective than the retrofit of the Bardenpho process on the basis of total annual costs. In the largest conventional activated sludge plant evaluated, the least expensive Bardenpho retrofit was approximately twice as costly as chemical precipitation on the basis of total annual cost. The annual O&M costs of the Bardenpho retrofit in this situation were only half of the annual O&M costs of chemical precipitation. The higher total annual costs of the Bardenpho process retrofits are related to the high capital costs associated with the biological reactors required for the five-stage process in order to achieve complete nitrogen control. No nitrogen control is provided by the chemical precipitation technology.

A similar situation exists in retrofitting the model plants to achieve the lower phosphorus limit (0.3 mg/L). Chemical precipitation was the more cost-effective alternative in all cases, based on total annual costs. Bardenpho technology was approximately 32 percent more expensive in the conventional activated sludge retrofit situation at the largest scale evaluated. However, annual O&M costs of Bardenpho technology were 20 percent lower than annual O&M costs of chemical precipitation in this case.

UCT Retrofit Costs

The capital costs of the UCT process retrofits and the Bardenpho process retrofits were comparable in most situations. The cost savings associated with the reduced biological reactor requirements of the three-stage UCT process compared to the five-stage Bardenpho process appear to be negated by the costs associated with the additional internal recycle requirements of the UCT process. The annual O&M costs of the UCT process retrofits were generally higher than comparable costs of the Bardenpho process retrofits, as a result of the additional O&M costs associated with the additional recycle pumping.

The total annual costs of retrofitting the model plants to the UCT process are compared to the costs of retrofitting chemical precipitation technology in Figure 3. As was the case for the retrofit of Bardenpho technology, chemical precipitation technology was more cost-effective than UCT technology in all situations evaluated on the basis of retrofit total annual costs. Achieving the upper total phosphorus limit by retrofitting a conventional activated sludge plant of 36,400 m^3/d capacity with the UCT process was at least twice as expensive as retrofitting the same plant with chemical precipitation technology. At the lower phosphorus limit, the cost advantage of the chemical precipitation process was reduced.

Based on the annual O&M costs of the retrofit, the UCT process became less expensive when the hydraulic capacity of the conventional activated sludge plant was between 4500 m^3/d and 13,600 m^3/d and the effluent phosphorus limit was 0.3 mg/L or if supplemental chemical addition was utilized instead of filtration to achieve an effluent phosphorus limit of 1.0 mg/L.

A/O Retrofit Costs

Retrofit of A/O technology to the model plants required considerably less capital expenditure than either of the other totally biological nutrient control options (Bardenpho or UCT) in all cases. The A/O process configuration included in the evaluation was a two-stage system, requiring considerably less tankage, mixing, aeration and recycle pumping than the five-stage Bardenpho process or the three-stage UCT process. In this configuration, no nitrogen removal is achieved by the A/O process; in fact, nitrification in the aerobic section of the A/O system must be avoided to prevent inhibition of phosphorus release under anaerobic conditions. The A/O process retrofit also resulted in the lowest annual O&M costs of the three totally biological options, in all situations. The O&M costs associated with achieving nitrogen control in either Bardenpho or UCT systems is not a factor in the operation of the A/O process. In the conventional activated sludge plant at the largest hydraulic capacity, phosphorus removal to an effluent limit of 1.0 mg/L was achievable with an A/O retrofit including supplemental chemical addition at an incremental O&M cost of less than $1 per kg total phosphorus removed.

The total annual costs of retrofitting the model plants to the A/O process are compared to costs of retrofitting chemical precipitation technology in Figure 4. Based on total annual costs to achieve a 1.0 mg/L effluent total phosphorus limit, chemical phosphorus removal was more cost-effective than retrofitting to A/O technology in all situations except conventional activated sludge plants of hydraulic capacity in excess of approximately 13,600 m^3/d. Beyond this size range, A/O became more cost-effective if supplemental chemical addition was practised in lieu of effluent filtration. Similarly, A/O became more cost-effective than chemical precipitation in conventional activated sludge plants of hydraulic capacity greater than approximately 13,600 m^3/d when an effluent phosphorus limit of 0.3 mg/L was imposed on the system. The annual O&M costs of all A/O retrofits to the model conventional activated sludge plants were lower than comparable O&M costs of chemical precipitation technology irrespective of the method used to achieve an effluent phosphorus limit of 1.0 mg/L. The A/O process was somewhat more capital intensive than the chemical precipitation technology in all situations, which impacted on the total annual costs.

Phostrip Retrofit Costs

Capital costs of retrofitting Phostrip technology to achieve phosphorus control were sensitive to the effluent total phosphorus limit imposed on the process. Capital requirements increased by approximately 50 to 100 percent as the effluent phosphorus limit was reduced from 1.0 mg/L to 0.3 mg/L. The higher capital cost required to achieve the lower limit was primarily related to the addition of effluent filtration equipment to the Phostrip process flowsheet. In primary plant retrofit situations, the capital costs associated with Phostrip technology were higher than the costs associated with A/O technology but comparable to the costs of the Bardenpho process in most cases. Phostrip technology was less capital cost intensive than

Bardenpho in secondary treatment plant retrofits (conventional activated sludge and extended aeration), but generally involved a higher capital cost than A/O process retrofits. In terms of annual O&M costs, the Phostrip retrofits were the least cost-effective of the EBPR technologies evaluated except in the small capacity extended aeration plants.

The total annual costs of retrofitting the model plants to the Phostrip process are compared to the costs of retrofitting conventional chemical precipitation technology in Figure 5. In all situations, the Phostrip retrofit was more expensive than the chemical precipitation retrofit to achieve the same effluent total phosphorus limit, on the basis of total annual costs. Similarly, annual O&M costs of the Phostrip retrofits were higher in all cases than the annual O&M costs associated with the chemical precipitation technology, although the Phostrip O&M costs were less sensitive to the effluent total phosphorus limit than the O&M costs of conventional chemical precipitation technology.

OTHER FACTORS AFFECTING THE APPLICABILITY OF EBPR PROCESSES

Factors other than economics impact on the applicability of EBPR processes in retrofit situations. The limitations imposed on discharges of phosphorus and nitrogen, the wastewater characteristics, the types and sizes of existing facilities as well as the knowledge of and experience with EBPR processes compared to conventional chemical precipitation technology will affect the final process selection.

Effluent Phosphorus Limits

Where phosphorus removal requirements have been imposed in Ontario, the typical effluent concentration limit has been 1.0 mg/L, based on total phosphorus. However, it is recognized that site-specific conditions may dictate more stringent effluent requirements. The International Joint Commission's Phosphorus Management Strategies Task

Force has recommended that all future municipal point source discharges to the lower Great Lakes Basin should consider requirements for total phosphorus removals to concentrations on the order of 0.1 to 0.5 mg/L.

The technical review of EBPR processes demonstrated that Bardenpho, UCT and A/O technologies were capable of achieving an effluent total phosphorus concentration in the range from 1.0 to 2.0 mg/L without effluent polishing. Effluent phosphorus limits of 1.0 mg/L or less would require some combination of final effluent filtration and supplemental chemical addition. Effluent filtration was shown to be capital cost intensive, eliminating any O&M cost advantage associated with the EBPR processes. In situations where an effluent total phosphorus limit of 1.0 mg/L is imposed, Bardenpho, UCT and A/O are only cost competitive with conventional chemical precipitation technology if supplemental chemical addition is practised. Phostrip technology was not cost competitive with conventional technology achieving a 1.0 mg/L effluent total phosphorus limit, even though effluent filtration was not required with Phostrip.

The economic assessment demonstrated that when a more stringent effluent total phosphorus limit is imposed, the EBPR technologies become more cost competitive with the chemical precipitation process. In fact, in conventional activated sludge plants with hydraulic capacity of 36,400 m^3/d, A/O was the least cost retrofit option. The imposition of effluent total phosphorus limits of less than 1.0 mg/L will favour the implementation of EBPR processes as, under these circumstances, these technologies have an O&M cost advantage over the conventional chemical precipitation technology, particularly in conventional activated sludge plants.

Effluent Nitrogen Limits

Nitrogen control requirements have been imposed in Canada only on a site-specific basis in situations where the assimilative capacity of the receiving waters is limited. Typically, nitrogen limitations have been based on effluent ammonia concentrations to control dissolved oxygen depletion in the receiving waters due to the nitrogenous demand and to prevent ammonia toxicity to the receiving water biota. Requirements to achieve complete nitrogen control, which implies the implementation of denitrification, have not been widespread. To our knowledge, the only municipal treatment facilities presently required to achieve a total nitrogen limit are Orangeville, Ontario and Kelowna, British Columbia.

EBPR processes such as Bardenpho and UCT provide complete nitrogen control and, in fact, denitrification is a process requirement to ensure optimum phosphorus removal biologically. The higher capital and O&M costs of Bardenpho and UCT systems are associated with the additional costs of nitrifying and denitrifying the wastewater. Additional reactor volume and oxygen transfer capacity must be provided. In return for these higher costs, Bardenpho and UCT produce a higher quality effluent, in terms of the total nutrient load (nitrogen and phosphorus), than the other process options. However, in situations where nitrogen control is not a requirement, this benefit in effluent quality may not justify the higher cost of the technology.

The imposition of a nitrogen control requirement on an existing treatment facility will impact significantly on the cost analysis presented. Under these circumstances, the costs of the conventional technology will increase and may exceed the costs of the Bardenpho and UCT options. This cost analysis was not within the scope of this study. However, there is no doubt that in situations where nitrogen control requirements are imposed, the EBPR options which incorporate nitrogen control will become more favourable from a cost standpoint.

The cost analyses presented were based on a five-stage configuration and a two-stage A/O process configuration. Bardenpho systems can be designed in a three-stage configuration to meet less stringent effluent nitrogen limits. A/O systems can be designed in a three-stage configuration in situations where denitrification is required. The process configuration will have a significant impact on the relative capital and O&M costs of the individual EBPR options.

Wastewater Characteristics

EBPR processes, particularly those that incorporate nitrogen control, are more sensitive to the characteristics of the raw wastewater than conventional chemical precipitation processes. The EBPR processes require that the COD (BOD_5), TKN and phosphorus concentrations be present at certain minimum ratios (COD/TKN > 12 for Bardenpho and UCT; BOD_5/soluble P >10 for A/O).

Based on 1980 data for 90 Ontario water pollution control plants, the average COD/TKN ratio in Ontario wastewater is approximately 9.3 and fifty percent of Ontario plants have a COD/TKN ratio of less than approximately 7.8. Primary clarification would further reduce the COD/TKN ratio in the influent to the biological section of the plant as COD is removed to a greater extent in the primaries than TKN.

Further, wastewater in Ontario has a relatively low total phosphorus concentration as a result of the regulation of the phosphorus content of detergents. EBPR technology was largely developed in South Africa, where raw wastewater strengths are considerably higher than in Canada. Under these circumstances, the cost advantages of EBPR processes are more readily demonstrated. The O&M costs associated with conventional chemical precipitation technology are related to the chemical dosage requirement, which is a function of the influent phosphorus level. A cost sensitivity analysis demonstrated that a 100 percent increase in chemical dosage would result in an increase in annual O&M costs of as much as 22.8 percent in new plants, depending on plant size and effluent phosphorus limit. On the other hand, the O&M costs associated with totally biological EBPR processes are relatively independent of influent phosphorus concentration.

Wastewater characteristics in Canada, in general, do not favour the implementation of EBPR processes. More than fifty percent of Ontario plants would not be suitable for EBPR without supplementation of the influent COD, which would increase the cost of the EBPR process and add further complexity to the operation. In addition, the low raw wastewater phosphorus concentrations common in Canada reduce the cost advantages associated with EBPR processes.

Characteristics of Existing Wastewater Treatment Plants

The economic analysis demonstrated that EBPR processes are most cost-effective in retrofit situations where the existing facility is a conventional activated sludge plant with a hydraulic flow in excess of approximately 13.6 Ml/d. EBPR processes cannot compete economically with chemical precipitation in primary plants required to achieve an effluent limit of 1.0 mg/L. The majority of extended aeration plants are too small to provide an economic advantage to EBPR processes and, as package plants, are not particularly amenable to an EBPR process retrofit. In Ontario, there are 44 conventional activated sludge plants with design hydraulic capacities of 13.6 Ml/d or greater; however, the actual hydraulic loading on conventional activated sludge plants in Ontario is only 69 percent of design, on average. Therefore, some of the 44 Ontario plants identified above may not be operating at flows in excess 13.6 Ml/d.

EBPR processes are more susceptible to variations in hydraulic and strength variations in the raw wastewater than chemical precipitation processes. Flow equalization has been provided in many of the existing EBPR plants and appears to improve the consistency of process operation. Few existing treatment facilities have flow equalization capabilities. The provision of such facilities in an EBPR process retrofit would increase the capital cost beyond those developed in this assessment.

Newer examples of EBPR technology have also demonstrated the importance of process control and the need to minimize re-aeration of the wastewater upstream of the anaerobic reactor. In new plants, incorporation of these details in the design will not impact significantly on the overall plant costs. However, in retrofit situations, implementation of dissolved oxygen control and modifications to plant hydraulics to minimize re-aeration can represent significant cost items depending on plant hardware and configuration. These site-specific factors will have an impact on the cost-effectiveness of EBPR processes in conventional activated sludge plants which appear to be suitable for EBPR process retrofit on the basis of size and wastewater characteristics.

Sludge Management Implications

EBPR technologies are sensitive to the sludge handling processes applied to the phosphorus-rich waste biological solids. Anaerobic conditions favour the release of phosphorus from the sludge. In Ontario, most conventional activated sludge plants practise two-stage anaerobic digestion and digester supernatant recycle, with disposal of sludge to agricultural land. Province of Ontario guidelines for sewage sludge utilization on agricultural lands state that only 'processed' sludges are acceptable, where 'processed' sludge is defined as a sludge that has been treated by aerobic or anaerobic digestion, or by other means of stabilization.

The implementation of EBPR processes may require major changes to sludge management practices in an existing plant. The best approach to sludge handling will depend on the existing hardware, the existing disposal methodology and the local regulatory requirements. In this cost analysis, the EBPR processes were not unduly handicapped by the specification of capital and O&M intensive sludge handling processes. However, in any specific retrofit situation, sludge management may significantly impact on the costs of EBPR processes.

State of Development of Phosphorus Removal Technologies

Phosphorus removal by simultaneous chemical precipitation has been widely applied in Ontario for more than ten years. During that period, it has been shown to be a practical, simple technology which will consistently provide compliance with effluent requirements.

EBPR processes are relatively new to North America. To date, few examples of the technology have been capable of consistently meeting their design objectives. Design relationships are generally empirical and the biochemistry of the phosphorus-removal mechanisms are not completely understood. Provisions for supplemental chemical addition and/or effluent filtration are generally necessary unless extensive treatability data from pilot or full-scale tests are available to demonstrate process reliability. Even with extensive treatability data, the provision of supplemental chemical feed equipment as back-up to the EBPR process would be recommended. EBPR processes are considerably more complex than the conventional chemical precipitation technology, requiring increased operator knowledge, training and supervision and/or the implementation of on-line monitoring and control equipment. These factors may outweigh the economic advantages which have been shown to apply to EBPR processes in some situations.

Capital Funding Assistance

The economic analysis demonstrated that, in general, EBPR processes are more capital intensive than the conventional chemical precipitation technology, but result in lower annual O&M costs in conventional activated sludge retrofit situations. Overall, the total annual costs of the EBPR processes may be higher because the additional costs of financing the capital expenditure outweigh the advantages in terms of O&M costs. In many situations, grants or low-interest loans are provided to a municipality to cover part or all of the capital cost of treatment works. The availability of capital funding assistance will have a significant impact on the cost-effectiveness of EBPR processes.

SUMMARY AND CONCLUSIONS

- Based on total annual costs, none of the EBPR processes were cost competitive with chemical precipitation to an effluent total phosphorus limit of 1.0 mg/L when effluent filtration was practised. When supplemental chemical addition was practised in lieu of effluent filtration, the A/O process became the most cost-effective technology in conventional activated sludge plants at a hydraulic capacity in excess of approximately 14,000 m^3/d. All other EBPR options in the configurations evaluated were at least twice as expensive as chemical precipitation in retrofit situations when the effluent limit was 1.0 mg/L total phosphorus.

- In situations where the effluent total phosphorus limit was 0.3 mg/L, the EBPR options were more cost competitive with chemical precipitation, particularly in larger conventional activated sludge plant retrofits. However, in the configurations evaluated, only A/O was more cost-effective than chemical precipitation based on total annual costs.

- The annual O&M costs of all EBPR options with the exception of Phostrip were lower than O&M costs of chemical precipitation in conventional activated sludge plant retrofits at a hydraulic capacity of 36,400 m^3/d, regardless of effluent total phosphorus limit.

- EBPR and chemical precipitation should be considered as complementary processes. Ideally, EBPR facilities should be designed to biologically reduce the phosphorus content of the wastewater to a practical minimum and the residual phosphorus should be removed chemically to the prescribed effluent limit. Chemical back-up to the EBPR system would be recommended.

- Given the present situation in Canada in terms of effluent requirements, existing facilities and wastewater characteristics, the number of wastewater treatment plants which would be candidates for a retrofit of EBPR technology is very limited.

- Circumstances which would lead to more widespread implementation of EBPR technologies include the imposition of effluent total phosphorus limits of 0.5 mg/L or less, the imposition of nitrogen removal requirements, major increases in chemical costs, and the development of greater confidence in the performance of EBPR processes.

ACKNOWLEDGEMENTS

Credits

This work was sponsored by the Environmental Protection Service of Environment Canada. Bardenpho is a proprietary process, marketed by the EIMCO Process Machinery Division of Envirotech Corporation. A/O is a proprietary process, marketed by Air Products and Chemicals, Inc. Phostrip is a proprietary process, marketed by Biospherics Inc. The paper was originally presented at the 58th Annual Conference of the Water Pollution Control Federation, Kansas City, Missouri, October, 1985.

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TABLE 1. SIZES OF TREATMENT PLANTS EXAMINED FOR PROCESS RETROFITS

PLANT TYPE	FLOW (1000 m^3/d)		
	LOWER LEVEL	MIDRANGE LEVEL	UPPER LEVEL
Primary	2.3	9.1	36.4
Conventional Activated Sludge	4.5	13.6	36.4
Extended Aeration	0.91	1.6	3.2

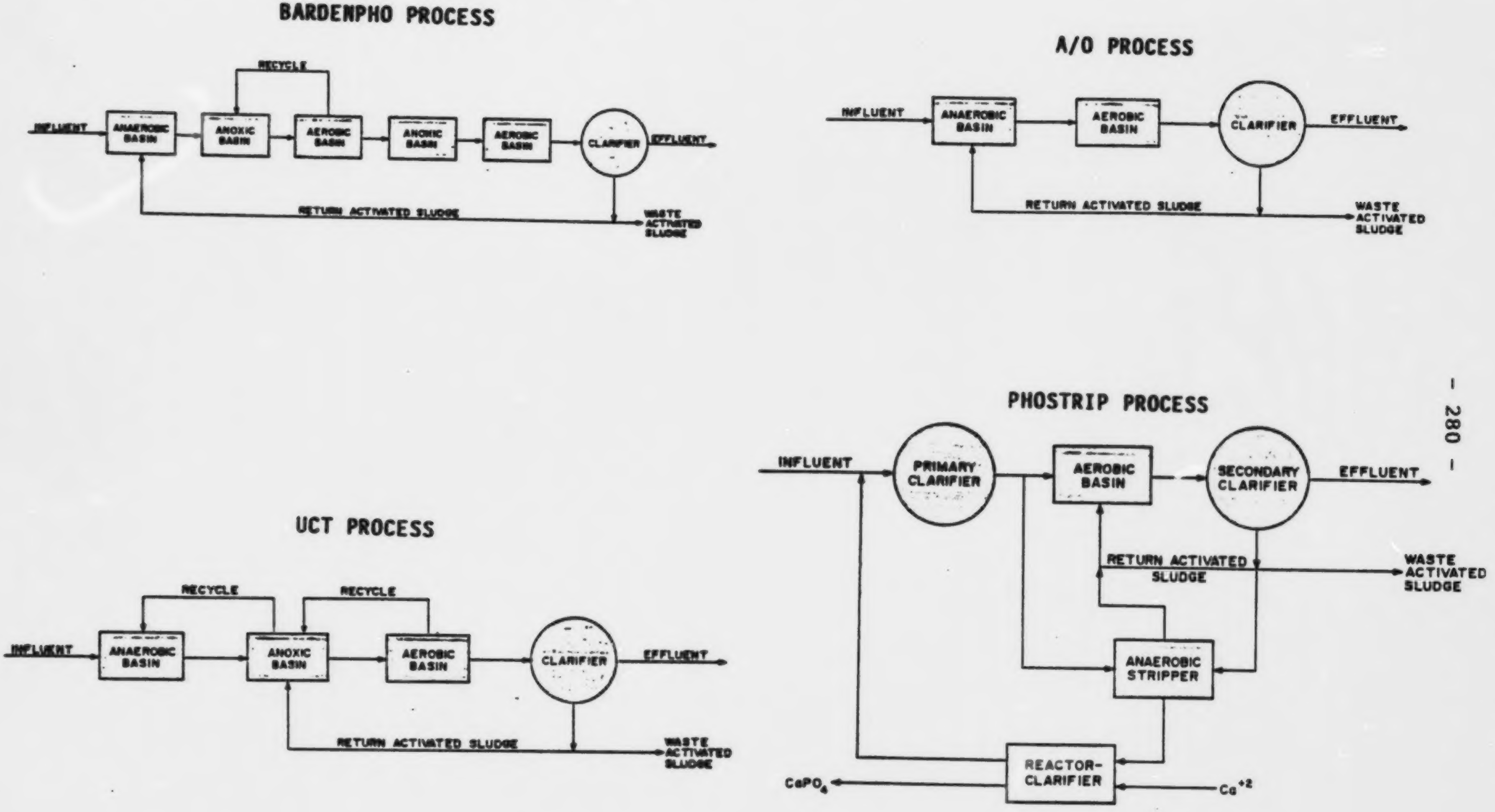
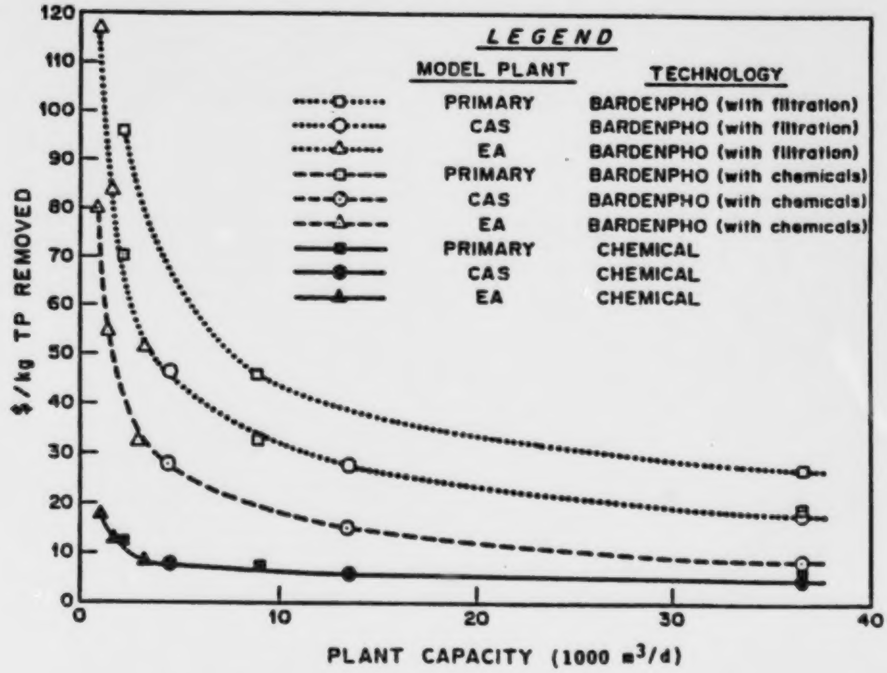
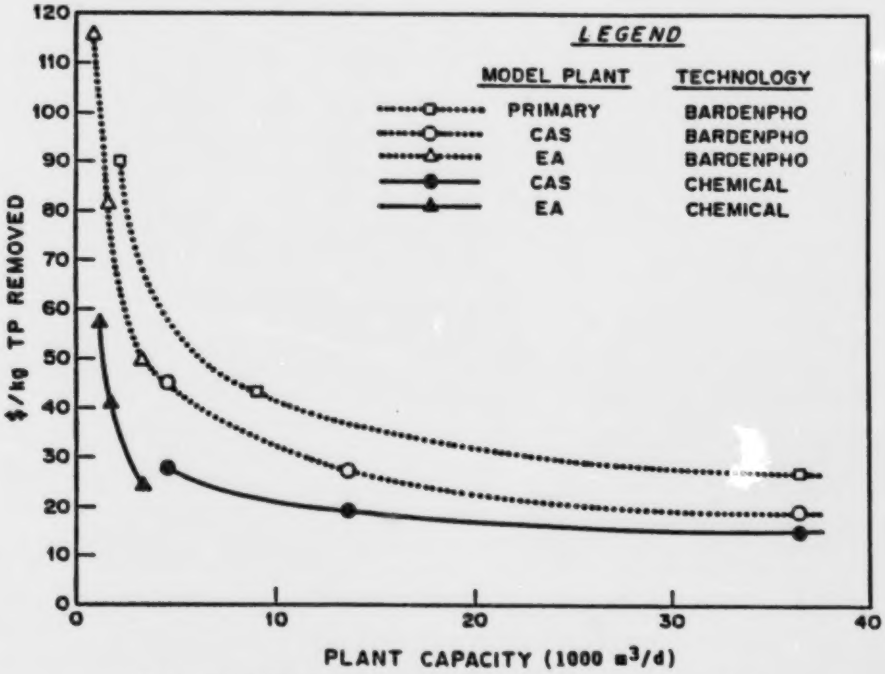

BARDENPHO PROCESS
RECYCLE
INFLUENT
ANAEROBIC BASIN
ANOXIC BASIN
AEROBIC BASIN
ANOXIC BASIN
AEROBIC BASIN
CLARIFIER
EFFLUENT
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE
A/O PROCESS
INFLUENT
ANAEROBIC BASIN
AEROBIC BASIN
CLARIFIER
EFFLUENT
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE
UCT PROCESS
RECYCLE
RECYCLE
INFLUENT
ANAEROBIC BASIN
ANOXIC BASIN
AEROBIC BASIN
CLARIFIER
EFFLUENT
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE
PHOSTRIP PROCESS
INFLUENT
PRIMARY CLARIFIER
AEROBIC BASIN
SECONDARY CLARIFIER
EFFLUENT
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE
ANAEROBIC STRIPPER
REACTOR-CLARIFIER
$CaPO_4$
Ca^{+2}

FIGURE 1: SCHEMATIC FLOWSHEET OF EBPR PROCESSES

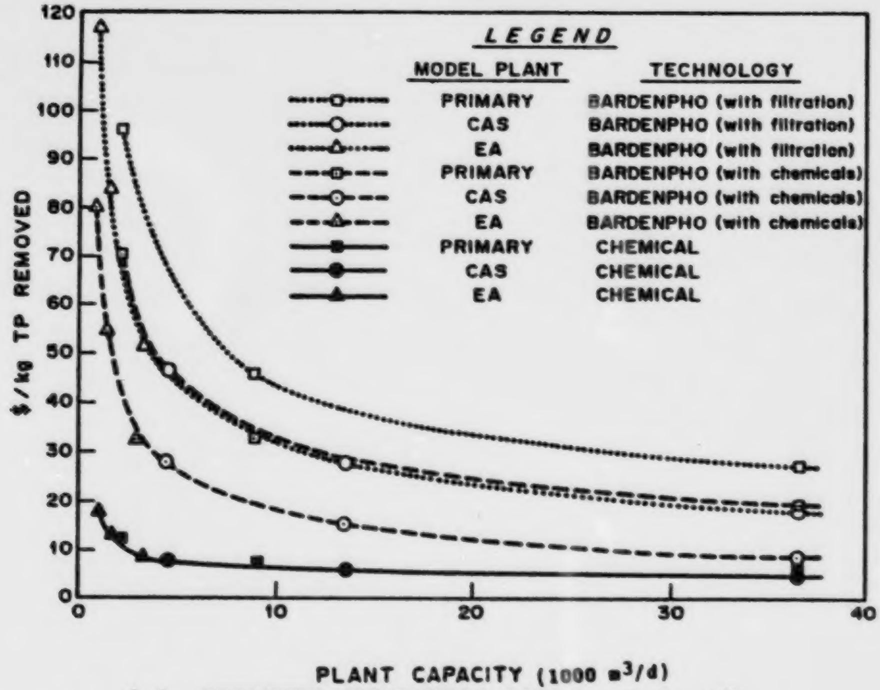


(a) EFFLUENT PHOSPHORUS LIMIT = 1.0 mg/L

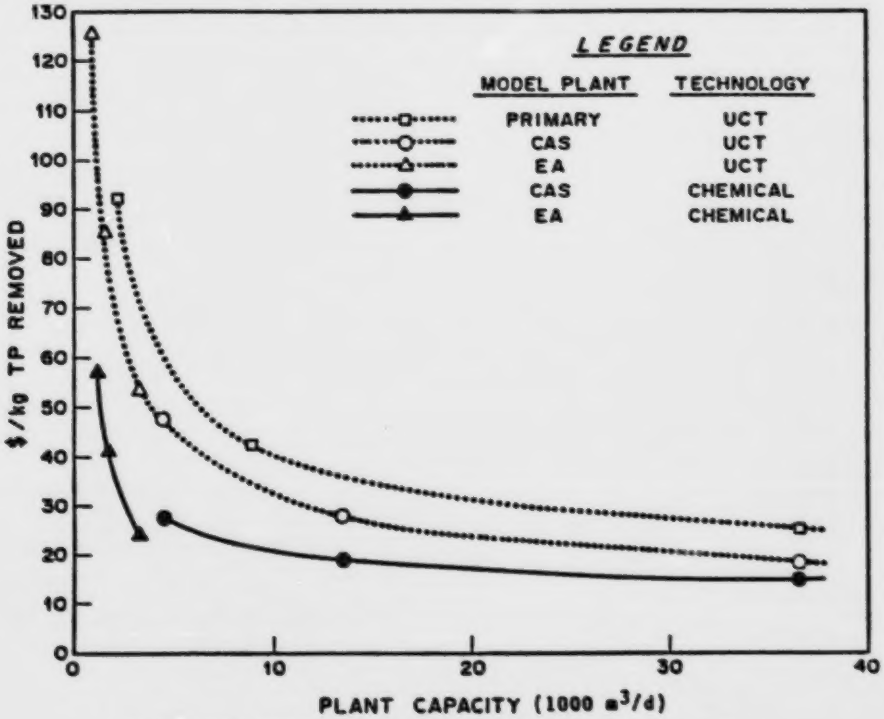


(b) EFFLUENT PHOSPHORUS LIMIT = 0.3 mg/L

FIGURE 2: COMPARISON OF RETROFIT TOTAL ANNUAL COSTS FOR BARDENPHO AND CHEMICAL PRECIPITATION TECHNOLOGIES

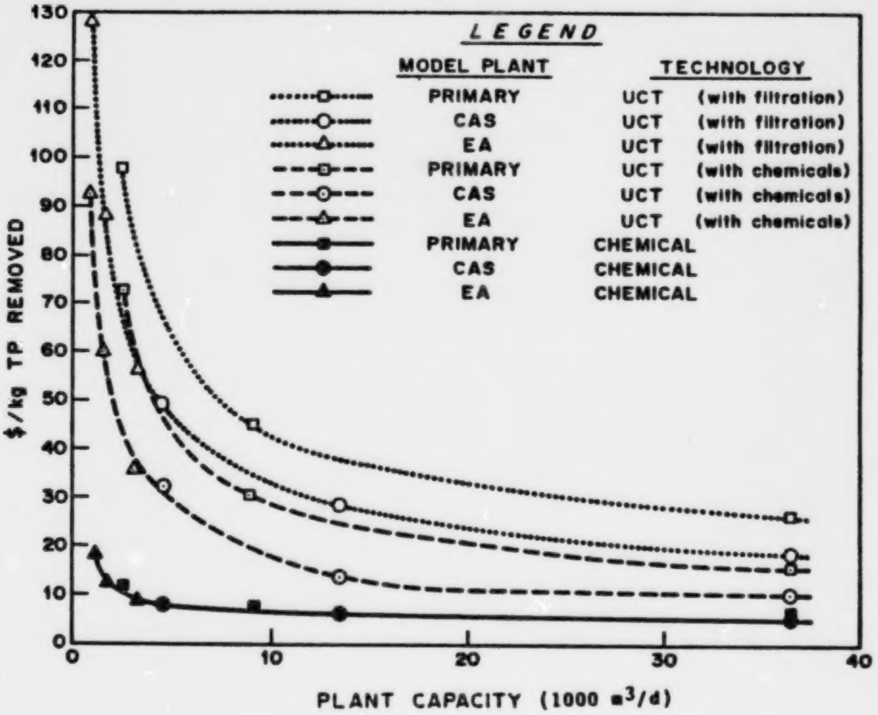


(a) EFFLUENT PHOSPHORUS LIMIT = 1.0 mg/L

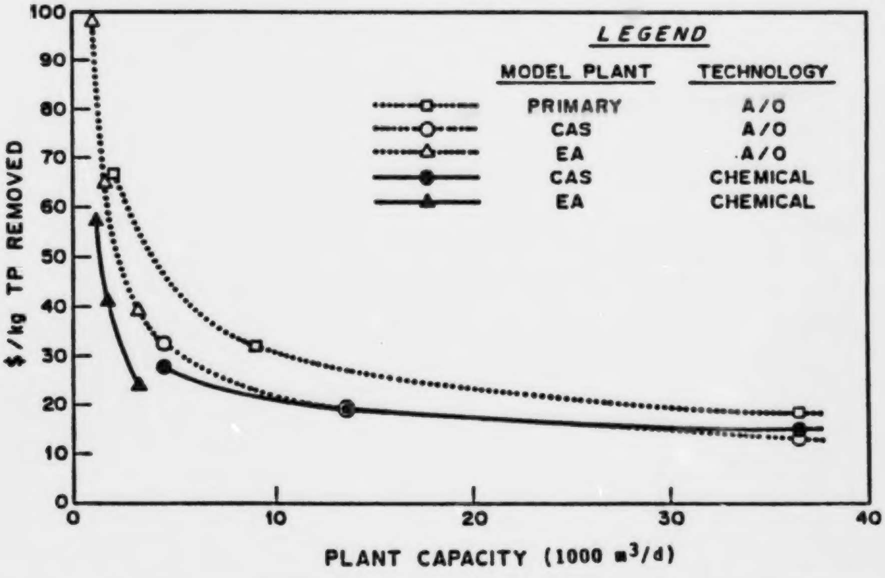


(b) EFFLUENT PHOSPHORUS LIMIT = 0.3 mg/L

FIGURE 3: COMPARISON OF RETROFIT TOTAL ANNUAL COSTS FOR UCT AND CHEMICAL PRECIPITATION TECHNOLOGIES

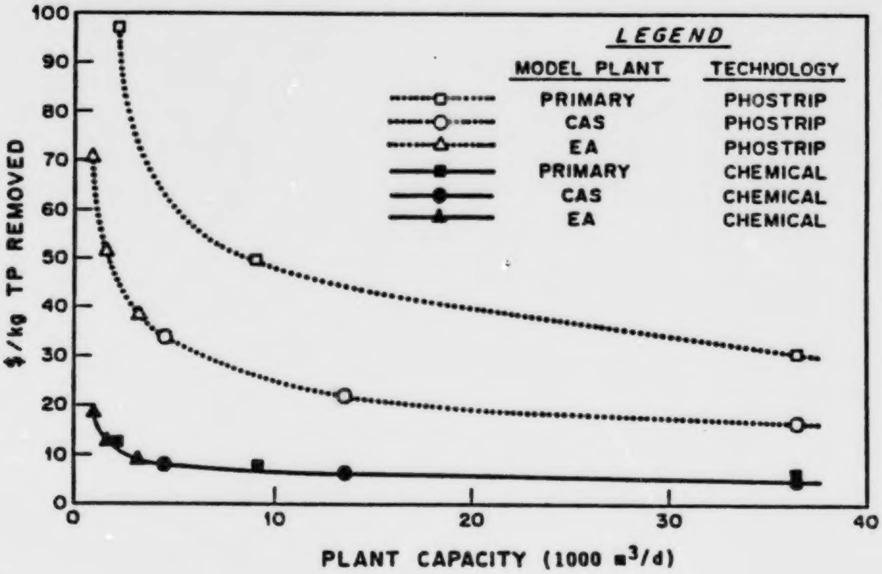


(a) EFFLUENT PHOSPHORUS LIMIT = 1.0 mg/L

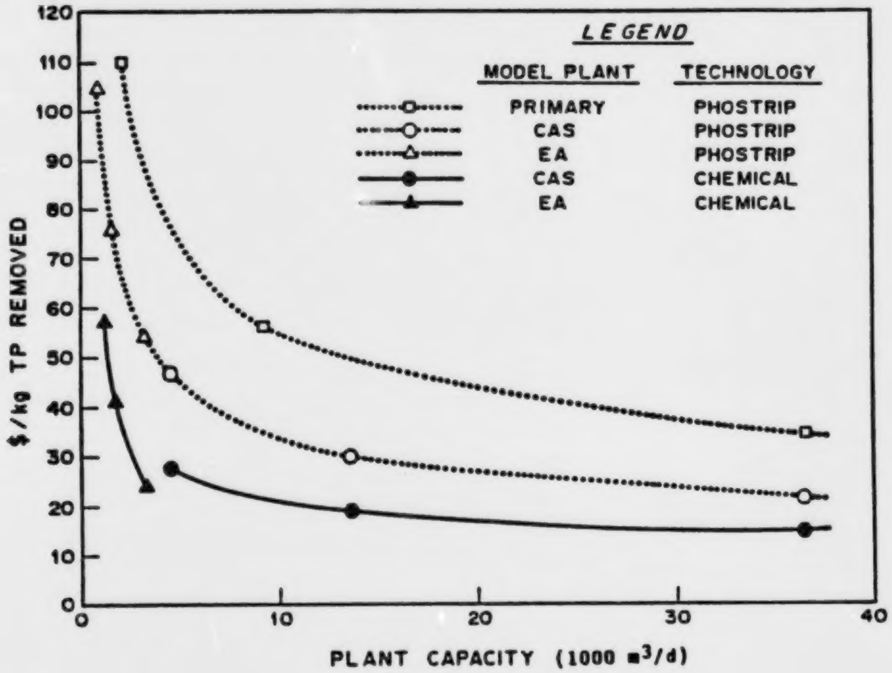


(b) EFFLUENT PHOSPHORUS LIMIT = 0.3 mg/L

FIGURE 4: COMPARISON OF RETROFIT TOTAL ANNUAL COSTS FOR A/O AND CHEMICAL PRECIPITATION TECHNOLOGIES



(a) EFFLUENT PHOSPHORUS LIMIT = 1.0 mg/L



(b) EFFLUENT PHOSPHORUS LIMIT = 0.3 mg/L

FIGURE 5: COMPARISON OF RETROFIT TOTAL ANNUAL COSTS FOR PHOSTRIP AND CHEMICAL PRECIPITATION TECHNOLOGIES

THE ASSESSMENT OF A POINT SOURCE DISCHARGE OF SUSPECTED MUTAGENIC AND CARCINOGENIC CONTAMINANTS: AN EPIDEMIOLOGICAL APPROACH

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Key words: Mutagenicity, Carcinogenicity, Genotoxicity, Epidemiology, Neoplasia, Fish, Hamilton Harbour.

ABSTRACT

This study was undertaken to correlate genotoxicity with variations in the incidence of neoplasia in wild fish populations. The frequency of genotoxic lesions in adults and embryos has yet to be determined. The frequencies of grossly visible "tumours" are reported for White suckers (*Catostomus commersoni*) from Lake Simcoe and Hamilton Harbour, as well as Brown bullheads (*Ictalurus nebulosus*) and Carp (*Cyprinus carpio*) from Long Point Bay and Hamilton Harbour.

White suckers had lip and skin tumours, as well as hyperplastic skin. A smaller number of liver and other tumours was also present. Fish from Hamilton Harbour had a 58.3% incidence of external lesions, versus 29% in the fish from Lake Simcoe. 14% of the fish from Hamilton Harbour had liver "lumps", 25% lipid changes, and 6.3% intestinal bumps, the fish from Lake Simcoe having frequencies of 21, 7, and 11.6% respectively.

Gonadal tumours were present in 4/5 of the carp/goldfish hybrids from Hamilton Harbour, versus 18/35 from Long Point. No other abnormalities were noted in these fish.

Bullheads possessed both external and liver abnormalities. External growths were present in 14% of the fish from Long Point, versus 48% in the fish from Hamilton Harbour. The only difference internally was a 7% frequency of liver lumps in fish from Hamilton Harbour, while none were present in the fish from Long Point.

Histological confirmation of this data is necessary before any valid conclusions can be made; however, a hypothesis that the fish from Hamilton Harbour are affected by carcinogenic contaminants appears to be reasonable, possibly in association with some other as yet undetermined factors. It remains to be seen whether such observations are of value in predicting the impact of carcinogenic/genotoxic chemicals on feral fish populations.

THE ASSESSMENT OF A POINT SOURCE DISCHARGE OF SUSPECTED MUTAGENIC AND CARCINOGENIC CONTAMINANTS: AN EPIDEMIOLOGICAL APPROACH

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ABSTRACT

White suckers (Catostommus commersoni) were captured during their spawning runs up Grindstone Cr., Burlington, Ont., and Whites Cr., Beaverton, Ont.. 225 Grindstone fish and 71 Whites Cr. fish were examined for external neoplasms, which the Grindstone fish possessed in higher numbers than the Whites Cr. samples (skin: 23.6 % versus 9.8 %). A large number of hyperplastic lesions were also present, again more frequently in the Grindstone fish. Grindstone fish also possessed a higher rate of lip neoplasia, predominantly benign papillomas (24% versus 7%). Gross observations of external neoplasms proved insufficient for their diagnosis, particularly in the case of presumed hyperplastic lesions.

Grindstone fish also possessed a significantly higher incidence of internal neoplasia, 4.1 %, in the 147 fish examined. 44 Whites Cr. fish were free of internal neoplasia. A wide variety of parasitic and infectious lesions of unknown etiology provided a great deal of "background noise", again making gross observations unreliable for neoplasia diagnosis. Chronic liver damage, as evidenced by hyperplasia, may have had a role in liver neoplasia induction; this hyperplasia may have been toxicant or parasite induced.

Genotoxicity data for the peripheral blood of control fish was not available for this paper, but will be presented orally. Variable damage (nuclear and micronuclei) was evident in fish from other areas. Grindstone fish had the lowest micronuclei incidence of three industrialized sites, but the highest incidence of abnormal nuclei. That these fish were at higher risk of developing neoplasia is evident. It is also possible that this risk is due in part to genotoxic chemicals in their environment, as evidenced by the induction of micronuclei in wild fish exposed chronically to industrial discharges.

INTRODUCTION

Mutagenic and carcinogenic chemical effects on both aquatic and terrestrial life are of increasing concern (Kraybill et al, 1977). This is because exposure is chronic, to low levels of complex mixtures, an exposure which can only be mimicked with difficulty in the laboratory. The only valid approach is epidemiological, with laboratory backup where appropriate. In this way, the populations at risk can be examined directly, to determine whether significant effects are evident. Investigators have reported several populations of fish felt to exhibit elevated neoplasia incidence due to discharged contaminants (Black, 1983; Smith et al, 1979; Pierce et al , 1978; 1980, Baumann et al, 1982; Grizzle et al, 1981; 1984; Kranz and Peters, 1985) While investigations such as these determine the risk of exposed populations, they fail to determine the cause of this risk, its source, or the consequences for the population as a whole, issues of considerable importance.

Chemical analysis of fish as well as sediment can serve to determine whether mammalian carcinogens are present (Baumann et al, 1982; Black, 1982; 1983; Grizzle et al, 1984), which have been tested in isolation with laboratory animals. Mutagenic activity can be detected with bacteria (Kinae et al, 1981; Osborne et al, 1982; Sloof and van Kreijl, 1982; Kurelec et al, 1981), or other short-term tests, again mimmicking mammalian exposure. Short-term testing for mutagenicity and/or genotoxicity can assess whether such activity is present and detectable directly in the exposed population, if appropriate techniques are available! Attempts to utilize this approach in a variety of ways have been somewhat successful (Prein et al, 1978; Hooftman and Vink, 1981; Alink, 1980), although a combination of risk assessment specifically in the population at risk, and testing in the laboratory for mutagenic or other activity (Stromberg et al, 1981; Black, 1983; Kinae et al, 1981) is necessary. However, the lack of a demonstrable correlation between elevated neoplasia risk, and detectable genotoxicity is of concern (Sloof, 1983). The use of genotoxicity in feral organisms has the potential to elimate a great deal of the laboratory effort which is being directed to screening complex effluents, allowing them to concentrate on the specific, active components. Of course, it must be kept in mind that the genotoxicity of mixtures in feral organisms, just as in laboratory systems, is largly unknown.

Many "tumour surveys" published have ignored complete patholgical examinations, concentrating only on "bumps", or assuming that grossly defined lesions are acceptable criteria for the diagnosis of neoplasia (Brown et al, 1973; Hard et al, 1979). Certainly, the failure of such papers to report their pathological findings is a serious ommision. We then sought to establish firstly whether a population of white suckers, previously reported to possess elevated neoplasia incidence (Sonstegard, 1977; Sonstegard and Leatherland, 1980) still feature such lesions, and whether secondly, they possess elevated genotoxic damage indicative of such exposure. The value of pathological examinations in diagnosis of neoplasia was also examined, in addition to its role in possibly understanding whether other factors may influence the induction and development of neoplasia.

MATERIALS AND METHODS

Fish thought to be at risk of developing neoplasia were sampled from a population spawning in Grindstone Cr., Burlington, Ontario. These fish spend a significant portion of their life in the Golden Horseshoe (industrialized) area of southern Ontario, the western basin of Lake Ontario and Hamilton Harbour in particular. A control population was sought at Long Point Bay, in Lake Erie, however this run was over at the time of the Grindstone run, therefor a population spawning in Whites Cr., Beaverton, Ontario, originating in Lake Simcoe, was substituted. This area is principally argricultural, with minimal heavy industrial or residential inputs.

Suckers were captured with 10-30 m. seines during the day, and returned in oxygenated, cooled water to the laboratory. Transport was in a 600 l. opaque tank, with approximatly 450 l. Guelph tap water, the loading rate not exceeding 75 fish per 600 l.. Transport time varied between 1 and 3 hours, and the fish were placed into a 2 m. diameter dark green fiberglass tank, containing 5000 l. Guelph tap water, with an approximate turnover time of 1 volume per hour. Temperature of this water is consistently 12 oC, with 75% oxygen saturation, though additional aeration was utilized.

Fish were sampled from Grindstone Cr. April 10, 11, 29 and May 6, approximately 70 fish per trip. Whites Cr. fish were all obtained (71) April 25, 1985. Autopsies were performed as soon as possible, though sampling of additional fish from the Humber and Oakville R. was carried out to provide additional specimens for histopathology and genotoxicity analysis. The final Grindstone fish was autopsied May 18, the final Whites Cr. fish the 29th, making a maximum of 5 weeks between capture and autopsy. Most fish were autopsied within 2 weeks of capture, though additional fish were added to the tank containing as yet unsampled fish, making it uncertain as to the exact duration of holding.

Fish destined for post-mortem were anaesthetized with MS-222, unless already dead. Fish often died overnight during the holding. These dead fish were examined externally, however internal examinations were not attempted. External lesions were recorded as to type, size and location, fish length and sex (when applicable), and any internal abnormalities also recorded. Any abnormalities were fixed in 10 % formalin or a Bouins solution (bony tissues), as well as normal tissues for comparison. Particular attention was paid to obtaining internal lesions for histopathology. A small sample of external lesions was obtained from the study fish, however early histopathological examination revealed their histopathology to be complex, hence the sampling of additional fish from the Oakville and Humber R.

Fixed tissues were routinely processed to paraffin, sectioned at 5 um., and stained with haemotoxylin and eosin for routine analysis. Tissues fixed in Bouins were subsequently retrimmed, post-fixed in ethanol (75%) and similarly processed. Where no abnormality was present in section, corresponding to a reported gross abnormality, this was recorded as "normal". In this instance then, barring the serial sectioning of complete paraffin blocks, the reported findings are obviously an underestimation of the true frequency of lesions. A common problem in diagnosing lesions in small tissues, or lesions small in size, is the orientation within the block.

Diagnosis were carried out by the first author almost exclusively, though some advise as to lesion diagnosis was made available by Dr. B.D. Hicks, of this laboratory. Where in doubt, the diagnosis made by the author was utilized. Lesions were classified as to their origin, tissue and lesion type (inflammation versus neoplasm). Differentiation between hyperplasia (controlled growth) and neoplasia (uncontrolled growth) was particularly difficult in skin and lip sections, hence morphologic criteria were adopted where appropriate, to aid in a diagnosis.

Genotoxicity was analyzed in peripheral blood obtained during autopsy from the heart. Blood was drawn up in a capillary tube, a drop placed on a slide, and this drawn out into a smear. After air drying, this was stained for 40 min. with 5% Giemsa, and scored blindly by an experienced scorer. Data obtained included micronuclei frequency, poylchromatic frequency and the frequency of abnormal nuclei, all relative to 2000 mature red blood cells. Attempts to score polychromatic (immature) nuclei in peripheral samples proved tedious, and were dropped, in favour of future analysis of kidney imprints. Scoring took place at 400-1000 X total magnification, and micronuclei were included when they were non-refractile, up to 1/5 the nuclear diameter, were stained similar to the nucleus, and contained some internal structure.

Statistics were limited to the Students T-test for the difference of means. Limited Chi-squared testing for the difference in incidence data was also performed, although the majority of incidence data was analyzed with a "common-sense" approach.

RESULTS

GROSS OBSERVATIONS: EXTERNAL LESIONS

296 fish were examined. Table 1 presents the biological data for the examined samples. Overall (sexes combined) the Grindstone fish were larger ($P < 0.01$). Females were consistantly larger than males in both samples, the sex ratio (1.54:1 for Grindstone versus 2.16;1 for Whites Cr.; Table 2) inducing the overall difference.

Two distinct skin abnormalities were observed on fish from both sites. Broad, usually flat, pale to white, firm areas, often found on fins as well as scaled areas, will hitherto be referred to as "plaques". It should be noted that this is merely a gross post-mortem (as opposed to histopatholgical) description. These lesions ranged upwards to several centimetres in diameter, and were raised up to 3mm. above the surrounding tissue. The edge of these lesions was usually well defined, and on cut surface these did not penetrate into the underlying tissues. "Papillomas" (again a gross post-mortem, descriptive term) were raised, hard, white structures up to 5 mm. in diameter. These differed from the plaques chiefly in their hardness, and small diameter relative to their height. These lesions also did not penetrate into the adjacent or underlying tissue. The presence of these lesions on top of scales made the preparation of histological samples difficult, as they would often slough off of the scales, and be difficult to section.

Lip lesions were also common in fish from both sites (Table

3). The normal lip, both upper and lower, of these fish featured a rugose appearance, is fleshy, white, soft and maleable. Lesions were normally hard, raised areas, obsuring the normal lip texture. On cut section these were continuous with the lip, however they often protruded up to 0.75 cm. above the lip surface, being up to 1.0 cm. in diameter. Multiple lip papillomas were common, often on the same lip, or on the corners.

Fish with external lesions of any kind were abundant in both sites. 58.5 % of the mature Grindstone fish were affected, versus 24.6 % of the Whites Cr. fish. These rates were significantly different ($P < 0.01$). The appearance of these lesions appears to be random, as affected fish were no particular sex, or size range (Tables 1 and 2). Fish with particular lesions were similarly sized, with the exception of female fish with lip papillomas from Grindstone, these being larger than unaffected females from the same river (Table 3). The frequency of specific lesions versus sex (Table 4) reflects a random infection, given the small sample size of females from Whites Cr.. The incidence of multiple lesions (Table 4 and 5) was consistantly higher in Grindstone fish. The statistical odds of fish having both plaques and papillomas, plaques and lip papillomas, both papillomas or all three lesions (for example 3.2, 8.6, 6.9, and 1.4% for Grindstone) are lower than the observed frequencies in both sites, indicating that affected fish run a higher risk of contracting a second affliction of a different type. This analysis ignores multiple lesions of the same type.

The distribution of skin lesions was almost entirely dorsal, except for a limited number of fin lesions (Table 5). Lip papillomas showed site differences, particularly in the shift from upper lips in Whites Cr. to the lower lip in Grindstone (Table 5). In addition, 8 % of the Grindstone fish had lip lesions in apposition, lending credence to the theory of an infectious etiology, as does the elevated frequency of multiple lesions in affected fish. Overall, the Grindstone fish had more lesions (368/225 fish) and a larger proportion on their lips (40.7 %) than the Whites Cr. fish (43/71 fish, 25.6 % on the lips) .

Table 1: Biological data for White Suckers, including average lengths (cm. (n=)) of all fish (A) and of affected fish (B). Note the absence of differences between sites of individual sexes, the between site differences being due to a small sample of females from Whites Cr.

A)

	Sites	
	Grindstone	Whites
Overall	40.9 (225)a	39.5 (71)a
Males	38.9 (136)b	38.7 (51)c
Females	44.2 (88)b	42.6 (18)c
Immature and not sexed	37.0 (1)	30.5 (2)

B)

	Grindstone	Whites
Infected: Overall	40.9 (131)	39.8 (17)
Males	39.1 (87)	38.7 (12)
Females	44.5 (44)	42.6 (5)
Uninfected: Overall	41.1 (93)	39.6 (52)
Males	38.7 (49)	38.7 (39)
Females	43.7 (44)	42.6 (13)

a,b,c: Significantly different, Students T-test, P. < 0.01

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Table 2: Sex ratios, both overall and for affected/unaffected fish by site and combined sites. Both data sets indicate a limited trend for males to infected more often than females.

	Grindstone	Combined	Whites
Male:Female Sex Ratio			
Overall	1.54:1	1.76:1	2.83:1
Infected	1.97:1	2.02:1	2.40:1
Uninfected	1.11:1	1.54:1	3.00:1
Infection Rate: Overall	58.5%		24.6%
Males	63.9%	52.9%	23.5%
Females	50.0%	46.2%	27.7%

Table 3: Average lengths (cm. (n=)) of fish infected with particular lesions, irrespective of sex (A) and by lesions and sex (B) for the two study sites. Uninfected fish were different lengths in the two samples, reflecting the overall trend noted (Table 1). Only females with lip papillomas were larger than uninfected fish of the same sex.

Lesions	Grindstone Cr.	Whites Cr.
A)		
Plaques	41.1 (45)	39.0 (6)
Papillomas	40.8 (36)	38.8 (5)
Lip papillomas	41.1 (97)	39.8 (11)
Uninfected*	41.1 (94)a	39.5 (53)a

*) includes 1 immature Grindstone fish, and 2 immature Whites fish
a) Significantly different, Students T-test, P < 0.05.

B)

	Males	Females	Males	Females
Plaques	39.5(31)	44.8(14)	40.3(3)	45.0(1)
Papillomas	39.4(23)	43.3(13)	38.8(5)	——(0)
Lip Papillomas	39.1(67)	45.6(30)a	38.6(7)	42.0(4)
Unaffected	38.7(49)	43.8(44)a	38.7(39)	42.6(13)

a) Significantly different, Students T-test, P < 0.01

Table 4: The infection rates (%) of seperate and combined (M+F) sexes of various skin lesions (A). Those bearing multiple types of lesions irregardless of sex are contained in B (infection rate (%; N=)). Note the frequency of multiple lesions of different types in fish from Grindstone is higher.

A) Infection	Grindstone			Whites		
	Males	M+F	Females	Males	M+F	Females
Plaques	22.8	20.0	15.9	5.8	8.5a	5.5
Papillomas	16.9	16.0	14.7	9.8	7.0	0.0
Lip Papillomas	49.3	43.1	34.1	13.7	15.5	22.2
Uninfected	36.0	41.7	50.0	76.5	74.6	72.2

a) does not include 2 immature plaque bearing fish

B) Infection	Grindstone	Whites
Plaques + Papillomas	7.5(7)	1.4(1)
Plaques + Lip Paps.	10.2(23)	2.8(2)
Both Papillomas	5.7(13)	1.4(1)
All three lesions	3.1(7)	1.4(1)

Table 5: The bodily distribution of lesions are contained as a percentage ((%) n=) of the total incidence of that lesion (I) and (II) the incidence of multiple lesions ((%) n=) at those sites . Unpaired and paired refer to fins, apposition to two lip tumours on opposite lips (kissing). Note the higher incidence of multiple lesions (of the same type)in Grindstone fish.

	Grindstonea		Whites	
	I	II	I	II
Plaques				
Bodyb	72.7(40)	52.7(29)	100(5)	0.0(0)
Unpaired	5.5 (3)	3.6(2)	0.0(0)	0.0(0)
Paired	21.8(12)	14.5(8)	0.0(0)	0.0(0)
Papillomas				
Body	65.8(25)	47.4(18)	71.4(5)	42.8(3)
Unpaired	21.1(8)	5.2(2)	14.3(1)	14.3(1)
Paired	13.1(5)	5.2(2)	14.3(1)	14.3(1)
Lip Papillomas				
Lower	53.6(67)	14.4(18)	36.4(4)	0.0(0)
Upper	35.2(44)	15.2(19)	63.6(7)	9.1(1)
Apposition	8.0(10)	8.0(10)	0.0(0)	0.0(0)
Corner	3.2(4)	0.0(0)	0.0(0)	0.0(0)

a) includes some fish sampled specifically to determine gross distribution, which were not autopsied, but were held for observation, a total of 254 fish making up the sample

b) all afflicted the dorsal body surface, with the exception of fins, and one fish with plaques(2) on the ventral scaled area

HISTOPATHOLOGY: SKIN AND LIP LESIONS

Normal epithelium on both scaled and unscaled (head and fins) areas consists of 10-20 layers of Malpigian cells, a keratinizing squamous epithelium. In this type of epithelium, the cells flatten out and die as they migrate to the surface from the principal mitotic region, adjacent to the dermis. At the junction of these two areas, the basal lamina, a secreted acellular membrane, is found. Scales, when present, project within a pocket of dermis from the dermis, hvaing a thinner overlying epidermis, which has no blood vessels as such. Commonly, both mucous cells and club (fright) cells are present as secondary components. These cells also originate deep within the epidermis, and mucous cells migrate to the surface to discharge their contents.

Epidermal lesion histopathology was based on a sample of fish from 4 rivers (106 total). The lesions of the epidermis were principally hyperplastic in character. The mildest lesions were a simple thickening of the malpigian layer, with the obliteration of the secondary cells. Hyperplasia was often broad based, and hence was initially felt to correspond with the grossly observed plaques. The majority of mitosis observed were in the basal area of the thickened tissue, corresonding to the normal mitotic area in control sections. This layer may however be variably thickened, and prominent in some lesions. Many of these hyperplastic lesions featured hyperplastic margins, which included the secondary cells, which were often enlarged (cytomegaly) and hyperplastic as well. A subtle transition to papillomas (the histopathological term for a benign neoplasm of epidermis featuring foldings of the dermis and epidermis) was visible, in that many hyperplastic lesions contained a scalloped basal lamina, or hyperplasia of the epidermis investing the ventral scale surface. In the majority of these hyperplastic lesions the cytology of the malpigian cells was normal, however as the depth and frequency of the dermal interdigitations increased (pegging), the cells often featured prominent nucleoli, often multiple, now visible because the chromatin was peripheralized in the nucleus. The cells however were still showing the normal migration pattern, increased eosinophilia with maturation as they flattened near the surface. In many lesions, increased numbers of pyknotic and karyorrhexic cells (dead) were visible, and tissue lymphocytes were often present, particularly in association with the mitotic region.

If the pegging of the basal lamina was significant (the criteria utilized in this study was that its depth be more than two times its width, in either direction), "hyperplastic" lesions were considered to be irreversable, hence they were classified as papillomas histologically. Grossly defined papillomas resembled merely very focal hyperplasia, in that the cytology of these tissues resembled that of normal epitheliun, however the majority featured significant pegging. Some papillomas were isolated on top of scales, however more aggressive ones appeared to lyse the scale material, and penetrate deeper into the epidermis. On unscaled areas, and lips, all papillomas featured extensive pegging into the dermis, whereas on scaled areas, quite often the pegging occured on top of a scale, hence the dermis was forced to penetrate into the epidermis. Many papillomas, whether featuring diffuse or focal hyperplasia, contained a more homogenous mitotic pattern, in that more "active" cells were visible in central regions of the pegs. In many cases, the mitotic region in pegs faced at right angles to the surface, and as such cells couldn't be expected to mature normally. Many cells within the pegs appeared to be mitotic, and this may in part be responsable for the penetration of epidermis into dermis. Alternativly, the pegging observed may be a compensatory response to increase the surface area of contact with the basal lamina, and hence the nutrition available to the now thickened epidermis.

While papillomas appear to be focal grossly, histologically many feature a somewhat diffuse growth pattern, in that normally several to many pegs are forming at once. If truly focal, arising from a single clone of cells, it is likely that a single peg, or pegs arising in an isolated area, would be formed. In contrast, the observed hyperplasia of malpigian and secondary cells adjacent to the focal papilloma lend support to a more diffuse pattern of growth. It is possible however that this adjacent hyperplasia is compensatory, in that no secondary cells are present in the papilloma, and mucous secretions in particular are critical to the animals health.

In some papillomas, the malpigian cells appear to be very aggressive, being basophilic, variable in size, both nuclear and total, often with multiple nucleoli, and varied in shape. Some pegs feature oval to stellate cells, dramatically different from the normal round cells. Single cell necrosis and inflammation are often present, indicating that mitotic activity may be enhanced in this region. Mitotic figures are however still uncommon in these lesion. Of concern when diagnosing papillomas, and differentiating them from hyperplasia, is the sectioning of samples. Given the hyperplastic margin on many papillomas, and their often small size, sections through the adjacent tissue could resemble hyperplasia, leading to a missed diagnosis. This may have been the case in the 2 papillomas which exhibited only hyperplasia histologically.

Normal sucker lips also feature a stratified squamous epitheliumn, without secondary cells. Taste buds appear to be the only secondary structure present. The basal lamina of lips is normally peged, due to the external configuration of the lips, hence the diagnosis of lip papillomas rested on the demonstration of a significant alteration in their number, size and extension into the dermis. If the relationship of the dermis and epidermis was essentially unchanged, in the presence of a thicker epidermis, this was defined as hyperplasia, normally increasing the basal lamina surface area little if any.

As such, hyperplasia was present in many sections, however the predominent lesion was a papilloma. The hyperplastic lesions, just as in the skin, featured normal cytology, while the lip papillomas featured a variety of cytology, definable as well, moderatly and poorly differentiated cells. These descriptive terms corresponded to increasing basophilia, diffuse mitotic activity, etc., all characteristics of skin papillomas. Invasiveness was evident in a single lip papilloma. In general, most papillomas were moderatly differentiated, both the Grindstone and Whites Cr. fish featureing some poorly defined lesions, however a marked difference was evident between hyperplastic lesions and papillomas, more of the latter being poorly differentiated, lending credence to the irreversability of this type of lesion.

Malignancy, leading to a definition of squamous cell carcinoma, was characterized by invasiveness, although limited evidence was present for metastasis in a single fish. Malignant lesions were present on fins (2), eye, operculum, lip (1 each) and scaled skin (2). Diagnosis of invasiveness implied that the basal lamina had been breached (or not excreted ?) by the epidermis, hence the malpigian cells were invading the underlying dermis. This was often difficult to detect, due to oblique sectioning, making the visualization of the basal lamina difficult. 6 of the 7 "cancers" arose from large lumps, or papillomas, a single cancer arising from a hyperplastic fin lesion. The growth pattern of these lesions was diffuse, with prominent dermal inflammation, intense basophilia, nuclear pleomorphism, chromatin peripheralization, nucleoli prominence, and wide variability in cell size. Cell shape was also variable, in particular stellate cells with a diffuse chromatin being common. The single possible case of metastasis (fish #77) featured cancer of the eye as well as skin.

HISTOPATHOLOGY: COMPARATIVE

In all, 106 skin samples, including 45 Grindstone, 8 Whites Cr., and some from both Oakville and Humber R.'s were examined. 18 grossly defined papillomas, plus 88 grossly defined plaques made up this sample. 16/18 papillomas were indeed neoplastic, as were 31/88 plaques, one being malignant. Overall then, 17% of the sample was grossly felt to be neoplastic, while histologically, 39.6% were in fact neoplastic. Only 2/18 lesions diagnosed as neoplastic grossly were hyperplastic, possibly due to sectioning as discussed earlier.

A total of 61 samples were subsequently examined further, 48 neoplastic and 13 hyperplastic. Interestingly, the pegging observed in these samples was equally split between dermis and epidermis as the "aggressor". Cytological criteria proved to be of qualitative but not quantitative value in confirming objective observations and diagnosis. Nuclear chromatin peripheralization was present in 100 % of the malignancies, and 40 and 38 % of the papillomas or hyperplasias. Semi-quantitative analysis of organization and basophilia revealed that malignances were more basophilic and less organized than the other types of lesions, however this was of little value in seperating these last two types. In summary, no magical criteria were evident to simplify lesion diagnosis. The diagnosis of neoplasia in sucker skin was predominently based on the epithelial behaviour, and its relationship with the dermis. Similar observations were made for lips.

Not all Grindstone and Whites Cr. lesions were examined histologically (53/411 skin lesions (12.9%) and 71/108 lip lesions (65.7 %)). Neoplasia was diagnosed directly in 16 skin samples (3 malignant) from Grindstone, versus 5 from Whites Cr.. Similarly, neoplasia was diagnosed directly in 40 Grindstone lip lesions, 5 Whites Cr. lesions. Extrapolating the ratios found in these samples (108 skin samples from 4 sites and 71 lip lesions only from the two study sites of interest) predicts that 119 skin papillomas, 99 hyperplastic lesions, 54 lip papillomas and 27 lip hyperplasia's would be present in the Grindstone sample. Similarly, 17 skin papillomas, 15 skin hyperplasias, 5 lip hyperplasia's and 5 lip papillomas would be found. Thus, by accounting for multiple infections, assuming one neoplastic lesion of each type per fish, 53 Grindstone fish would have skin neoplasia (23.6%) versus 7 Whites Cr. fish (9.8%). 24% of the Grindstone fish would have lip neoplasia, versus 7 % of the Whites Cr. fish.

GROSS OBSERVATIONS : LIVER LESIONS

Normal sucker liver is a diffuse, reddish-brown organ which surrounds the intestinal coils. The large gall bladder is situated ventro-lateral to the main liver mass, though the liver has several large masses attached to various points of the intestine. Colouration of the livers varied widely between fish, however pale foci were common within livers; several fish had bright green liver lobes as well. Grossly discernable liver bumps were found in many fish, although early post-mortems in particular mistook multifocal endocrine structures of unknown character,normally attached to the intestine immediately posterior to the oesophagus, as neoplasia. Bumps of unknown etiology were normally hard, pale, oval to spherical, continuous with the liver parenchyma, and ranged upwards to 1 cm. diameter. The pale foci were normally indistinguishable from the normal liver except for colour (texture, etc.), ranging up to several cm. in diameter.

147 Grindstone fish were examined internally, plus 44 Whites Cr. fish. 26.5% and 6.8 % respectivly featured pale foci; the sex of these fish, particularly in the Grindstone sample, was more often female than in the overall sample (47.7 % versus 39 %). Green livers were found in 5 (3.4%) of the Grindstone fish, 4 being males. 16.3 % of the Grindstone fish had lumps, versus 18.2% in the Whites Cr. fish. Many of these proved to be endocrine.

HISTOPATHOLOGY: LIVER

Sucker livers are homogenous, featuring double rows of liver parenchymal cells forming chords, separated by the hepatic sinusoid, through which the blood filters. Bile cannuliculi invest each parencymal cell, joining to form distinctive bile ducts, with low cuboidal epithelium. Arteries and central veins are present, often in conjunction with the bile ducts. Pancreas tissue is normally on the periphery of the liver, and in surronding mesentary, however it may also invest some of the larger bile ducts. The liver parenchyma cell is moderatly basophilic, with a large nucleus, centrally located, with a prominent nucleolus. Vacuoles (lipid or glycogen) often invest these cells, making the cells appear disorganized, however this appears to be a function of diet. In most instances, the levels of lipid are homogenous throughout the liver.

Elevated numbers of macrophage were evident in several control fish, however they were very prominent in all fish with green livers. These macrophage contained a yellow-brown pigment, which may have been ceroid, a lipid breakdown product. Of the fish examined for various lesions, the rate of occurrence of this was similar to background, however 8/11 livers with complicating disorders possessed elevated numbers of these cells.

Pale foci proved to be due in large part to lipid variations within the liver. Two fish exhibited bile duct neoplasms, specifically cholangiomas (benign). These featured large numbers of relatively normal bile-duct like tubules, often with minimal supporting strom, surrounded by a clear line of dermacation from normal liver. Additional biliary hyperplastic or fibroplastic changes were evident in 7 Grindstone livers, while cholangitus/-peri-biliary hepatitus was present in several tissues. Hyperplasia of liver parenchyma was also evident in a few samples.

Liver bumps often featured parasitic changes, which were common in many pale livers as well. Fatty changes and endocrine structures also accounted for many of these grossly observed lesions. The Grindstone fish featured the majority of hyperplastic or neoplastic changes. Hepatocellular hyperplasia was present in 5/23 Grindstone samples, only a single Whites Cr. fish featuring bile duct hyperplasia. A single cholangioma was found in a Grindstone fish, similar to those found in pale foci.

Bile duct hyperplasia, an increase in the numbers of small bile ducts, was a common finding. These were incidental observations in general as such lesions couldn't be observed grossly unless extreme. This lesion is of interest as it may be a precursor to the cholangiomas seen. Bile duct hyperplasia was seen in 16 % of normal livers viewed, indicating a possible relationship with the spawning process. Only 8 % of pale livers and 6 % of livers with bumps had this condition, though 40 % (2/5) green livers were afflicted. An examination of all liver sections available (controls plus grossly affected livers, 82 from Grindstone, 21 from Whites Cr.) revealed a higher incidence in Whites Cr. fish (13% versus 5 %) than in Grindstone fish. An examination of additional liver tissue will be undertaken to resolve this apparent lack of correlation with the presence of cholangiomas.

Hepatocellular hyperplasia is often considered a preneoplastic change as well, even though no hepatocellular neoplasms were found in this study. Increased basophilia in hyperplastic nodules is the most common form, with reduced lipid levels and sinusoidal compression. The nucleolus is often prominent and cytomegaly may be present. Hepatocellular hyperplasia, either focal (nodules) or multifocal to diffusely focal were noted in 9.7% of the 82 Grindstone livers examined, none being found in Whites Cr. fish. This condition was absent from control fish, being most common in fish with bumps. While it would appear that this phenomenon is restricted to Grindstone fish, additional samples are necessary to confirm this.

Liver neoplasia was found in 4 fish from Grindstone Cr. (the fourth, to be described later, was a malignant bile duct tumour listed as an intestinal serosal mass; fish #'s 11, 35, 210 and 385), none in Whites Cr.. Two of these (210 and 385) featured a low cuboidal, normal appearing epithelium forming tubules, with some congestion in the minimal stroma present. Both were small, and well encapsulated, though extensive macrophage numbers were present in adjacent tissue. The cholangioma from 210 also featured small islands of hepatocytes, whereas 385 contained only bile duct elements. Fish 35 contained a very large cholangioma, with nests of tubules seperated by bands of connective tissue, containing inflammatory cells (lymphocytes and macrophage). The lack of a capsule, or clear demarcation from normal liver tissue may indicate invasiveness, hence malignancy, though it was a well differentiated lesion. Fish #11's lesion was a focal, invasive nest of oval to stellate cells with homogenous nuclei, showing little tendancy to form tubules. Islands of degenerate liver cells had been isolated by the invasion of surrounding tissue, though no inflammation was evident. This lesion appears to be a poorly differentiated biliary neoplasm, in part because of the presence of rodlet cells and was classified as a cholangiocellular carcinoma. Thus, the four hepatic neoplasms seen in Grindstone fish were all biliary, and were split 50/50 between benign and malignant.

GROSS OBSERVATIONS: MISCELLANEOUS LESIONS

Diptheritic-like cardiac membranes were common, in company with small (1 mm.) hard white cysts on the hearts surface. 42.3 % of the Grindstone fish were affected, versus 25% of the Whites Cr. fish. The membrane was soft, pale, often fluid filled, whereas the cysts were embedded in the hearts surface. Lesions resembling neoplasms were common on the intestinal serosa, less so in the mucosa. Both types were hard, pale on cross section, and well demarcated, varying up to 0.5 cm. No significant lesions were found in other organs.

Parasites were common in these fish, including the presumed parasites infecting the heart. Philometra in the fins was common (26.6% in Grindstone, 14% in Whites Cr.), particularly in the pectoral fins. Pleurocercoids in the peritoneum, possibly Ligula sp., were found rarely (3.4% in Grindstone, 6.8% in Whites Cr.), as were gill copepods, intestinal acanthocephalens and epithelial "clams". Mesenteric or serosal multiple grossly visible granulomas were common (13% in Grindstone, 11% in Whites Cr.), which were propably a result of parasite passage.

HISTOPATHOLOGY: MISCELLANEOUS LESIONS

Three (3) neoplasms were found in fish with miscellaneous lesions, including the previously described cholangioma (#35), which was originally observed on the intestinal serosa, undoubtably adhering during autopsy, though it invested large parts of the liver as well. Two neoplasms of intestinal mucosal origin were found (351 and 419). These featured glandular epithelial structures, in a variety of configurations, including papilliform (finger-like) cystic and tubular, with varying amounts of mucosal interstitium. The epithelium in 351 appeared reasonably normal, it forming limited tubules and cysts, and was diagnosed as an adenoma (benign). 419 on the other hand formed highly invasive fingers of very abnormal small, basophilic cells occassionally forming tubules, etc., featuring prominent nuclei and peripheralized chromatin. The lesion actively invaded the adjacent mucosa as well as hepatic tissue, being classified as an adenocarcinoma (malignant).

Inflammation due to presumed parasites (not often seen in section) was common, particularly in mesentary. Lymphocytic inflammation of peritoneal membranes, pancreas and adipose tissue was common. Granulomas (calcereous or collagenous areas originally containing macrophage) were also common, and many were large enough to be visible to the naked eye. Thus, many lesions in the peritoneum may have been parasitic. The heart lesion consisted of a fatty layer strongly attached to the pericardium with congested, and/or haemorrhaged areas. Calcereous foci with melanin aggregations were common, as were parasitic cysts containing the intermediate stages of digenetic trematods, the presumptive causative agent which was also visible grossly.

GENOTOXICITY

The use of peripheral Giemsa stained blood smears proved to be a reasonably easy to score system for detecting chromosome breakage. The normal mature erythrocyte (12 um.) is oval, with a central, basophilic, oval nucleus. It was feared that this nucleus (the nucleus is absent in mammalian cells) would obscure micronuclei if present, however quite a few were seen in preparations from three industrialized sites. Difficulties in staining yielded some slides with stain granules, which strongly resembled micronuclei, and it was for this reason that control data is unavailable, as the majority of these slides had to restained prior to analysis. Of a sample of 64 slides, 16 were not readable due to poor staining. 7/9 control site slides were among this group.

The micronuclei seen in peripheral blood cells (mature) strongly resembled those classically seen in immature, polychromatic erythrocytes in mammals. These were circular, on the same plane as the nucleus, stained similarly to the nucleus, and have some hint of internal structure, their size varying up to about 1/10 th the nuclear diameter. Micronuclei were present in 3/16 Grindstone Cr. slides, a total of 3, for an average of 0.1875 in 2000 examined erythrocytes. 15 slides from Humber R. fish yielded 4 slides with 5 micronuclei, and average of 0.33/2000. 15 Oakville Cr. slides yielded 5 slides containing 8 micronuclei, for an average of 0.53/2000. Only 2 Whites Cr. slides were suitable for examination, yielding no micronuclei.

Observations of abnormally shaped nuclei, including kidney, indented, bilobed and barbell shaped ones, were nade quite frequently. Overall, Grindstone had the highest frequency of these cells/2000 mature erythrocytes (3.625) followed by Oakville and Humber fish (1.8 and 1.6). The two Whites Cr. slides featured an average of 4 abnormal nuclei, though this was a very small sample.

As a measure of haematopoetic function and/or rate of red cell formation, the numbers of polychromatic cells /2000 mature cells was chosen. Little variability was evident between the three sites (Grindstone 22.9; Humber 27.5; Oakville 21.5) the two Whites Cr. slides yielding an average of 40, again based on a sample too small for testing.

Statistical treatment of this data will be presented, however it is interesting to note an approximate trebling between the highest and lowest sites of micronuclei data, with Grindstone the lowest, while the opposite was true of nuclear abnormality data. The incorporation of additional slides for controls and statistical analysis may aid in determining the significance of these values, though it is promising to note the between site variability.

DISCUSSION

It is readily apparent that the fish sampled from Grindstone Cr. were afflicted with a significantly higher number of papillomas/carcinomas, cholangiomas/ carcinomas, adenomas/carcinomas, and several types of parasites. The predominent lesion was the papillomatous conditions found on the lips and skin. Lesions such as these have been reported in passing to be found in White suckers (Black et al, 1980; Sonstegard, 1977). A more thorough account by Black (1983) of a survey in E. Lake Erie found lip papillomas in 5.3-9.3% of the fish from a variety of sites; elevated frequencies were not found in polluted sites. Reports by Sonstegard (1977) of elevated frequencies of Hamilton Harbour oral papillomas (29.6%) are unsubstantiated by adequate data, though he reports frequencies of 0.0-0.7% for control sites. Subsequent studies in this area by V. Cairns (Canadian Center for Inland Waters, Dept. of Fisheries and Oceans, Burlington, Ont.) have found the lip papilloma incidence in fish >40 cm. fork length to be 39% (n=1200). While the incidence in this study compared favorably with the data of Sonstegard (1977), it is lower than that found by Cairns (pers. comm.). This may be in part because he was selective for fish >40 cm. fork length, whereas the average total length for Grindstone fish in this study was only 40.9 cm. Studies by Cairns have concentrated on the Great Lakes, showing trends in papilloma incidence decreasing from the high point in Oakville Cr. (62%, n= 111) to lows of 0.0% in N. Lake Huron. The background (control) value of 7% found in this study for L. Simcoe fish compares favourably with many of Cairns sample sites, though no incidence data is available for L. Simcoe fish.

It is very interesting that both authors fail to provide information on the frequency of skin papillomas and other lesion, which were as frequent as lip papillomas in this study. It may have been that both authors, as initially thought in this study, felt plaques were merely hyperplastic, contributing little if any to skin neoplasia incidence, however the pathological examination of the fish in this study indicate the contrary. It may be that these lesions are exacerbated by the holding of affected fish prior to examination, a factor requiring further study. The shift in distribution from body to lips, suggested by Sonstegard (1977), appears to be evident when comparing the two samples from Grindstone and Whites Cr.. Certainly, the relationship between the skin and lip lesions bears further investigation, as does the failure of papillomas to be present on the ventral surface of the fish. If chemically mediated, skin lesions would be expected to be present on those tissues in contact with the sediment, including lips and fins as observed, but not on the dorsal surface as was so common.

The pathological lesions observed on the skin and lips are extremely similar to a family of lesions collectively called papillomatosis. Evidence for epidermal papillomata as a spontaneous or possibly virally induced lesion is numerous, in a variety of species (Bylund et al, 1980; Obradovic et al, 1983; Hussein and Mills, 1982; Chronwall, 1976). Evidence for the viral nature of such lesions in eel (Schwanz -Pfitzner, 1976; Peters and Peters, 1979; McAllister et al, 1977), cod (Jensen and Bloch, 1980) and walleye (Walker, 1969; Kelly et al, 1983) is circumstantial, but convincing. Particularly interesting is the apparent induction of epithelial neoplasia in salmon exposed to a herpesvirus, which also induced hepatic necrosis (Kimura et al, 1981). Spawing papillomatosis with evidence of virus has been seen in smelt (Anders and Moller, 1985), and indeed Sonstegard (1977) has suggested that a C-type, RNA virus is causative of the papillomas seen on spawning suckers. Preliminary examinations to date with direct and indirect Electron Microscopy have failed to produce evidence for virus in our studies. If indeed of viral etiology, the variations in papilloma incidence may be unrelated to chemical contamination of the sediment, possibly being related to fish density, sediment physical properties (abrasion ?) or simply variations in the numbers of pathogenic virus. Alternatively, chemicals may promote infection, by corroding the skin, reducing mucous production (an important anti-pathogen barrier in fish), or by reducing immune competance. Again, it is conceivable that virus induced hyperplasia provides a more active tissue with the potential to be altered by sediment-borne carcinogens. Little evidence is however available in support of any one of these possibilities.

The subsequent development of invasive, malignant skin lesions has not been reported for papillomatosis, and may bear further investigation. It is not innappropriate to assume that viral lesions couldn't progress to cancers, as seen in esocidae lymphosarcoma, however it is also possible that given appropriate stimuli, the ultimate result of any mitotic tissue would be cancer. Indeed, the induction of papillomas from hyperplasia in bullheads (Black 1982; 1983) by the application of sediment extracts (reportedly extremely caustic) supports the contention that continuous necrotizing exposure will select for cells capable of dividing faster, in an attempt to compensate for the damage. This would prove an excellent promoting factor in the devlopment of cancer from either mutagen induced foci, or spontaneously altered foci. In the context of continual, severe necrotizing insults such as solvent extracts (propably also knife edges if tested) applied to the skin, or in the case of fish exposed naturally to sediment-borne chemicals, any agent can be carcinogenic! Thus, environmental carcinogens must be defined as those capable of eliciting this growth at reasonably realistic and environmental levels of exposure.

The low, but significant incidence of cholangiomas/ cholangiocellular carcinomas in Grindstone fish is an uncommon finding in published studies. Dawe _et al_ (1964) found 3/12 suckers to possess such lesions, however they were unable to repeat their findings in a subsequent intensive survey (Dawe _et al_, 1976). Neither Black (1983) or Sonstegard (1977) reported such lesions, indeed internal lesions of any kind, though Black reported basophilic liver nodules in some of the 520 fish examined. The only report of such lesions is that by Baumann _et al_ (1982) of cholangiomas in brown bullheads (1.2% in <2 year old fish, 33% in >2). The vast majority of lesions induced in laboratory exposed fish are hepatocellular in nature, however these studies often involve high concentration, short term exposure, to immature or embryo stages, and may not be representative of chronic, environmental carcinogenesis. It may be that these lesions are a response to chronic toxicosis, and the excretion of toxic chemicals via bile, rather than directly to metabolites, such as may affect parenchyma. The presence of hepatocellular hyperplasia in Grindstone fish may indicate that such chemicals are present, however the evidence for this is scanty, and the failure of the Grindstone fish examined to feature bile duct hyperplasia is a serious complication.

In a similar vein, adenomas/adenocarcinomas are rare in laboratory studies, though several have been reported with Nitroso compounds (Khudolhy, 1984). Black (1983) has reported some in redhorse suckers, but no incidence data is given. It is very tempting to hypothesize that the adenomas/ carcinomas are induced by ingested carcinogens. The elevated parasite numbers seen in the Grindstone fish may have some bearing on both cholangiomas and adenomas. The large amount of inflammation and/or granulomas seen in many mesentaries and livers may be related to parasite migration patterns. As such, the heavy parasite burden of these fish may, through chronic necrosis, have a promoting influence on spontaneous or induced lesions in many tissues. While the high numbers of these organisms may be due to contaminants or immune-suppression, it is more likely that they reflect an eutrophic environment, with large populations of host available to promote infections. Elevated parasatism has not been noted in other studies to date, though they could be a factor.

Attempts to isolate the etiology of observed neoplasia in wild fish have often been by chemical means (Baumann et al, 1982; Black, 1982) though some authors (Grizzle et al, 1984; Tomita et al, 1978; Kinae et al, 1981) have combined in-vitro mutagenicity testing with the epidemiology of neoplastic fish. It is curious however that at least one waterbody contains demonstrated mutagenicity and/or genotoxicity , even in fish exposed to these water (Hooftman and Vink, 1981; Alink et al, 1980; Prein et al, 1978; Sloof and van Kreijl, 1982) without apparently inducing neoplasia in resident fish (Kurelec et al, 1981; Sloof, 1983). Genotoxicity has yet to be detected in resident fish with elevated neoplasia incidences, and it will become clear whether such a relationship is present in the samples obtained during this study. The variability between impacted sites is interesting, particularly in that V. Cairns (Pers. Comm.) has found that Oakville Cr. fish possessed a 62% incidence of oral papillomas (n=111), the site with the highest levels of micronuclei in the present study.

Genotoxicity analysis in feral fish is in its infancy, with few studies coming up with applicable approaches (Stromberg et al, 1981; Longwell and Hughes, 1980; see Landolt and Kocan, 1983). Techniques applicable to fish embryos may have value (Longweel and Hughes, 1980; Smith and Valli, 1984); indeed embryos from Grindstone and Whites Cr. fish have yet to be analyzed in this study. The measurement of genotoxicity in adult fish is more difficult, due to the slower overall rate of cell division. The detection of chromosome damage in long-lived cells may prove useful in chronically exposed fish. The induction of micronuclei, and abnormalities in erythrocyte nuclei, by mutagens in the laboratory indicates that such structures can be due to gentoxicity in wild fish (Hooftman and de Raat, 1982; Siboulet et al, 1984). Preliminary results (Dr. A.C. Longwell, National Marine Fisheries Service, Milford, Conn., Pers. Comm.) indicate that such structures are also visible in wild fish, however as yet they have'nt been linked to any increased propability of contracting neoplasia.

The results of this study suggest that the White suckers spawning in Grindstone Cr., and possibly exposed to industrial pollution, both point source in Hamilton Harbour, and diffusely in the Golden Horseshoe area of S. Ontario, have increased neoplasia rates, specifically epidermal, biliary and intestinal. The possible role of parasites, virus, sediment-borne chemicals, and habitat in general is discussed. Early results of genotoxicity analysis were inconclusive, however the possible impact and detection of genotoxicity and carcinogenic chemicals bears further study. Areas of future concern may be the devlopment of models for chronic sediment-borne carcinogen exposure, and predictive risk assessment in wild and laboratory fish exposed to genotoxic and carcinogenic chemicals. It appears, given the preliminary information in this report, that genotoxicity analysis in wild fish may be a sensitive monitor of environmental chemicals of this type, and such damage may be related to induced neoplasia in white suckers.

SUMMARY

Genotoxicity data was correlated with neoplasia incidence in wild fish populations exposed to suspected mutagenic and carcinogenic discharges. Data is presented for white sucker (*Catostomus commersoni*) neoplasia, genotoxicity and parasatism.

Grindstone Cr. fish (exposed) had lip and skin lesions (58.3 %) whereas the control fish (Whites Cr.) had only 29 % incidence. Grindstone fish had fewer liver lesions (14% versus 21%) and intestinal or other internal lesions (6.3 % versus 11 %), but had more hepatic colour changes (25% versus 7%). External lesions were randomly distributed between sexes and fish sizes, though multiple lesions were more frequent in Grindstone fish. This rate was higher than the statistical odds of such an event, hence infected fish may run a higher risk of subsequent infection. A predilection for the upper lips in Whites Cr., versus lower in Grindstone, and for increased lip infection generally in Grindstone (40.7 % of all lesions, versus 25.6 %) may indicate contaminant induced shifts. Only Grindstone fish (10) had lip papillomas in apposition.

External lesions were predominantly hyperplastic histologically. Many (31/88) grossly hyperplastic growths featured significant interdigitation of the basal lamina, and as such were classified as benign papillomas. Skin papillomas were normally benign (12/18), though several (4/18) were invasive, and were classified as malignancies. A single grossly hyperplastic lesion was malignant, as was an opercular mass. The estimated overall

skin neoplasia frequency in Grindstone was 23.6%, versus 9.8 % in Whites Cr. fish.

Lip papillomas were examined from 71 fish (61 Grindstone, the remainder Whites Cr.). The majority 40 (65%) were benign, however 20 (33%) were merely hyperplastic, while 1 (1.6%) was malignant (invasive). The incidence in Whites Cr. fish was 7, 7 and 0% respectivly. The estimated overall lip neoplasia rate for Grindstone fish was 24.4%, including one malignancy, versus 7% in Whites Cr..

Numerous (147 Grindstone, 44 Whites) fish were post-mortemed internally. Pale foci and green livers exhibited uneven lipid distribution and large numbers of macrophage. Parasites accounted for the majority of diagnosed liver lumps (Grindstone 16.3 %, Whites 18.8%). Four (4) biliary neoplasms were found in Grindstone fish, two being malignant. Hepatocellular or biliary hyperplasia was common.

A wide variety of parasitic granulomas were present in internal organs (12.9 % Grinstone, 11.4 % Whites) as was inflammation. Two (2) intestinal neoplasms (one malignant) were present in Grindstone fish. Diptheritic membranes (cardiac) due to cestode metacercarie were common (42.3 % in Grindstone, 25 % in Whites). Philometra, an external parasite, was also more common in Grindstone fish (26.6 % versus 14 %).

The genotoxicity data for the control site was not available for this paper. Data for three analyzed sites (Oakville, Humber and Grindstone) varied in micronuclei numbers (0.53, 0.33 and 0.18 respectively). Grindstone fish did possess higher levels of abnormal nuclei than Oakville or Humber fish (3.6 versus 1.8 and 1.6 respectively), while the mitotic indexes were similar.

Overall, Grindstone fish featured higher rates of external (23.6%), lip (24.4%) and internal (4.1 %) neoplasms, parastism and hepatocellular hyperplasia. Bile duct hyperplasia, presumed to be a precursor of the biliary neoplasm common in Grindstone fish, was more common in Whites Cr. fish, and may reflect inadequate sample sizes, or the effects of spawning. The presence of suspected carcinogenic and/or mutagenic discharges may be in part responsable for the increased neoplasia incidence in Grindstone fish, in combination it is felt, with chronic toxicosis, and/or viral infection.

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DEVELOPMENT OF PREDICTIVE ORGANIC CONTAMINANT STRUCTURE-PROPERTY-TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS

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Key words: Toxicity, Organics, Aquatic Organisms, Hazardous Contaminants.

ABSTRACT

Aquatic ecosystems and water supplies are exposed to a large number of organic contaminants. Traditional chemical-by-chemical toxicity testing methods are often too slow and expensive to permit all chemicals to be tested. Thus there is an incentive to estimate or predict toxicity from chemical structure using Quantitative Structure Activity Relationships (QSARS).

In this study, acute lethal toxicity tests are being conducted with two small crustaceans, *Daphnia Magna* and *Artemia*, and the results are correlated with the chemicals, properties and structure. The chemicals studied include PCBs, chlorophenols, chlorobenzenes, hydrocarbons, and series of nitrogen and sulfur heterocyclic aromatics and polynuclear aromatic hydrocarbons.

The results obtained indicate that the acute toxicity of non-polar organics is primarily controlled by the organism-water partitioning characteristics of the chemical, which is a reflection of aqueous solubility. Mathematical descriptions of this partitioning-toxicity phenomenon are being developed which, it is hoped, will find application to the prediction of the toxicity of various chemicals.

In a complementary study, the photo-induced toxicity of anthracene to *Daphnia* has been investigated. The results indicate that the primary toxicant is an active (probably free radical) species formed in or on the organism.

DEVELOPMENT OF PREDICTIVE ORGANIC CONTAMINANT STRUCTURE-PROPERTY TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS

by

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ABSTRACT

A quantitative structure-activity relationship (QSAR) model is proposed describing the behaviour and effects of organic contaminants as they partition from water into small aquatic organisms. Experimental 48h-LC50 data are reported for several classes of organic pollutants and two test organisms, *Daphnia magna* and *Artemia*. Relationships are established between the acute lethal toxicity of these chemicals, aqueous solubility, and octanol-water partition coefficient. The results indicate that in this case toxicity is non-specific and primarily controlled by organism-water partitioning. Preliminary work on the phototoxicity of anthracene is discussed and the limits of the structure-toxicity relationship are shown through a comparison of toxicity test results across chemical classes. Inherent in both theoretical and empirical work is the assumption of a common toxic mechanism and a 1:1 relationship between octanol-water partition coefficient (K_{OW}) and the bioconcentration factor.

Abstract

A quantitative structure-activity relationship (QSAR) model is proposed describing the behaviour and effects of organic contaminants as they partition from water into small aquatic organisms. Experimental 48h-LC50 data are reported for several classes of organic pollutants and two test organisms, *Daphnia magna* and *Artemia*. Relationships are established between the acute lethal toxicity of these chemicals, aqueous solubility, and octanol-water partition coefficient. The results indicate that in this case toxicity is non-specific and primarily controlled by organism-water partitioning. Preliminary work on the phototoxicity of anthracene is discussed and the limits of the structure-toxicity relationship are shown through a comparison of toxicity test results across chemical classes. Inherent in both theoretical and empirical work is the assumption of a common toxic mechanism and a 1:1 relationship between octanol-water partition coefficient (K_{OW}) and the bioconcentration factor.

Introduction

Aquatic ecosystems are presently being exposed to thousands of organic contaminants from a variety of diffuse and point sources. Chemicals such as pesticides, hydrocarbons and chlorinated hydrocarbons from product use, effluents, spills, and runoff can be acutely toxic to aquatic organisms and as importantly can bio-accumulate to levels many times higher than ambient concentrations.

Traditional toxicity testing cannot provide the rapid hazard assessment (initial screening) necessary for regulatory pruposes. Hence procedures to estimate or predict the potential for toxicity and bio-accumulation based on the chemical structure are invaluable as a means of by-passing the need to conduct extensive and expensive experimental tests.

The objective of this study at the University of Toronto is to develop improved methods by which information about the chemical structure of an organic contaminant can be used to estimate physical-chemical properties, organism uptake rates, and toxic effects. Such quantitative structure-activity relationships (QSAR's) have proven highly useful in drug and pesticide research and development (Hermens et al., 1985). Our approach is to proceed down two parallel paths. First is a modelling effort in which we propose models or equations describing the behaviour and effects of these chemicals as they partition from water into small aquatic organisms. Often these models are initially tested on data from other workers. Essentially, the model provides a testing hypothesis. Second are experimental studies in which the model results are tested or the model is calibrated. Often the inability of the model to describe the data reflects an inherent misconception which must be corrected by modifying the model to reflect the actual processes more faithfully.

In this paper we briefly outline the QSAR model hypotheses and describe the experimental work which is proceeding in parallel. The experimental work consists of short-term acute lethal toxicity tests developed specifically for organic contaminants and two larval micro-crustaceans, *Daphnia magna* in freshwater and *Artemia* in saltwater. We also describe some phototoxicity tests.

Model

We believe that the key processes are the equilibria and kinetics of organism-water partitioning. The equilibria for non-metabolized substances are reasonably well described by the octanol-water partition coefficient K_{OW}, or by aqueous solubility. We find that the chemical solubility in the organism is relatively constant and typically 1% to 10% of the solubility in octanol. This latter solubility is fairly constant for hydrophobic organic chemicals. It appears that the dominant process is simply partitioning into organism lipids which are similar to octanol in properties and constitute (effectively) 1% to 10% of the organism's volume. This model has been successfully used as a basis of correlation for bioconcentration factors in fish.

We also believe that the concentration in the critical target tissue of the organism at which mortality occurs is relatively constant for a series of similar chemicals. The ratio of this tissue concentration to the water concentration which yields the tissue concentration (e.g. the LC50) is some multiple or a partition coefficient. The magnitude of this multiple is clearly similar or proportional to that of the other partition coefficients of octanol-water and organism-water. It follows that the LC50 tends to be a fairly constant fraction of the water solubility for liquid chemicals, or more specifically, the subcooled liquid solubility for solids.

This concept is perhaps best illustrated numerically in Table 1 in which the toxic and bioconcentration concentrations are compared for two chemicals of K_{OW} 1000 and 10000.

It is clear from Table 1 that the best test of this hypothesis is to compare values of LC50/solubility or equivalently plot log LC50 versus solubility (expecting a line of slope 1.0) or calculate values of LC50.K_{OW} or equivalents plot log LC50 versus K_{OW} (expecting a slope of -1.0).

A further discussion of these concepts has been published recently by Bobra et al. (1983, 1985) as part of this study. Figure 1 is an attempt to depict these relationships.

These concepts imply that equilibrium has been reached, i.e. the uptake time is short compared to the test time. We have extended the work of Mackay and Hughes (1984) for fish uptake times to apply to smaller organisms, but it appears that for all practical purposes, equilibrium is reached in our test systems. It may become necessary to include a kinetic "correction" expressing

Table 1. Illustrative calculation of the partitioning behaviour of two chemicals (arbitrary units).

PHASE	CHEMICAL A		CHEMICAL B	
	Concentration	Ratio	Concentration	Ratio
saturated octanol	1000	1000 (K_{OW})	1000	10000 (K_{OW})
saturated water i.e. solubility	1		0.1	
fish	0.050	50 (ie. .05 K_{OW})	0.5	500 (ie. .05 K_{OW})
lake water	.001		.001	
organism tissue	100	1000 (approx. K_{OW})	100	10000 (approx. K_{OW})
LC50 in water	.01		0.01	
LC50 solubility		0.1		0.1
LC50 x K_{OW}		100		100

the increase of critical tissue concentration as a function of time.

This hypothesis can also be used to predict the toxicity of mixtures. For example in the case of Table 1, the tissue concentration of 100 could also be a 50-50 mixture of A and B, for example a water solution of 0.05 of A would give a tissue concentration of 50 which could be augmented by 50 of B from a water solution of 0.005 to give a total of 100. The addiitivity hypothesis is then that the sum of the individual contributions is 100. It can be shown that this is equivalent to a statement that the sum of the terms (Concentration/LC50) be unity, which has been previously proposed (by Finney (1942) and others) as the additive toxicity hypothesis. When this hypothesis is not satisfied it is likely that the mechanisms of action of the toxicants differ.

We are also undertaking work to include a probability term in the equation which would enable the percent mortality to be estimated at concentrations other than the LC50.

Methods Development and Rationale

The test protocols have been outlined in Bobra et al., (1983) for Daphnia and Wells et al., (1982) for Artemia. The object was to expose test organisms to known, constant concentrations of pure single organic compounds in aqueous solution. Care was taken to avoid emulsion formation in stock solutions and exposure chambers, and especially to minimize loss of toxicant from solution by volatilization. The latter problem likely represents the major uncontrolled variable responsible for widely varying toxicity values reported in previous studies using open exposure chambers (Bobra et al., 1985).

Young or larval stages of aquatic organisms, especially crustaceans, have proven to be the most sensitive stage in the life cycle (Vanhaeke et al.,1980). Micro-crustaceans are particularly suitable for evaluating "physical toxicity" (O'Brien, 1967) because of their very high surface area to volume ratio. Their ability to use cutaneous diffusion for respiration and excretion is possible because of this intimate contact with the external environment. When exposed to a constant concentration of water-borne toxicant, equilibrium between water and organism concentration and the resultant toxic effect should be rapidly achieved and maintained. Thus differences in metabolic detoxification or protein binding capacity for slowly metabolized non-specific toxicants will not greatly modify the internal concentration and toxic effect (Hermens et al., 1985). Hence physical-chemical properties of the toxicant which determine the extent of this partitioning process will (it is hypothesised) determine toxicity.

EXPERIMENTAL RESULTS

The test chemicals, selected physical-chemical properties, and median lethal concentrations (LC50's) are listed in Tables 2 and 3 for Daphnia and Artemia. 95% confidence limits around the LC50 point estimates were very similar for both test organisms and all compounds except chlorophenols. Average values within compound classes for both animals were ± a factor of 1.22 for chlorobenzenes; ±1.26 for PCB's; ±1.40 for chlorophenols; ±1.24 for azaarenes; ±1.21 for chlorinated methanes. The higher values for chlorophenols reflect the significantly shallower slopes of the dose-response curves.

Chlorinated Aromatics

Figures 2 and 3 are plots of the dependence of LC50's on the aqueous solubility (hydrophobicity) of the tested compounds. The theoretical sub-cooled liquid solubility rather than the actual (lower) solid solubility was used since it is believed to be the "correct" correlating parameter, being more related to both the chemical's partitioning tendency into an organic phase (Miller et al., 1985) and the thermodynamic activity at the site of action, or "effective dose" (Ferguson, 1939). Also previous experimental toxicity data show that LC50's expressed as fractions of the sub-cooled liquid solubility are more accurate single parameter predictors of toxicity (Abernethy, 1985).

Thus plots of LC50 versus solubility or K_{OW} (an empirical measure or model of water-organism partitioning) are expressing the same structure-activity relationship. The use of K_{OW} is preferable when solubility data is unavailable or suspect, while using solubility will highlight the "cut-off" phenomenon of very hydrophobic organics, which despite a high K_{OW} cannot achieve a water concentration sufficient to deliver the higher effective dose.

The intercept of an LC50 versus solubility regression line is a measure of the inherent sensitivity of the test organism under specific exposure conditions (Hermens et al., 1985). Here Daphnia was more sensitive to chlorinated aromatics than Artemia although both test results support the hypothesis that the product of bioconcentration factor (K_{OW}) and LC50 was relatively constant, i.e. the resulting internal concentrations are about the same for equi-toxic conditions. Points lying on the 45° degree line (LC50 = water solubility) indicate compounds which were "non-toxic". These higher homologs (large molar volume) have a very low water solubility ("cut-off" phenomena) and may also have a lower solubility in the target biophase, which may be manifested as a higher fraction of the liquid or sub-cooled liquid solubility required to exert the toxic effect (Bobra et al., 1985). Eventually the water solubility limit is reached and the compounds are "non-toxic".

It is evident from the graphs that chlorobenzene and PCB toxicity is a well-behaved function of solubility. In contrast the relationship for chlorophenols was less well-defined. As ionizable substances, chlorophenol structure-acivity relationships require the introduction of the dissociation constant (pK_a) as a second variable (Konemann and Musch, 1981). Both ionized and unionized forms may be toxic but the latter form probably has a higher uptake and elimination rate as suggested by increased toxicity of chlorophenols at lower external pH values (Konemann and Musch, 1981). Internal pH will influence the elimination rate, and hence the net bio-accumulation.

Mono-Substituted Benzenes

Toxicity data from the tables and previous unpublished work (Abernethy et al., 1985), permit a ranking of LC50's for benzene and four mono-substituted derivatives based on both Daphnia and Artemia results, which were the same: benzene $\leq$ nitrobenzene $\leq$ phenol < toluene < chlorobenzene, in order of increasing toxicity. This further illustrates the close correlation between the two tests. However the order of toxicity observed for these compounds and young stages of fish and amphibians varied considerably from each other and was different from that observed here. In addition, no correlation was evident here or in other studies (Birge et al., 1985) between LC50's and K_{OW}'s.

While physical-chemical properties and toxicities within a class of compounds such as the chlorobenzenes tend to be well-behaved functions of molecular descriptors such as molecular volume, mass, area, or number of chlorine atoms, different substitutents change the relevant physical-chemical properties more or less than the corresponding change in molecular weight. This makes the structure-property relationship less amenable to prediction. Thus differences in bioconcentration and toxicity will correlate better with molecular weight variations due to the addition of single structural units (e.g. benzene rings) but not from adding different substitutents (Southworth et al., 1978).

Simple, single parameter correlations (toxicity versus K_{OW}) across chemical classes are also less successful due to biochemical differences in metabolism, steric or other interactions modifying the toxicity (Schultz et al., 1980).

Azaarenes

These are polynuclear heterocyclic bases containing a single basic nitrogen within an aromatic ring system. Effluents from coking and coal-based synthetic liquid fuel production as well as certain petrochemical activities contain polycyclic bases in complex mixtures of organic compounds (Southworth et al., 1978).

Three representative compounds, ranging from 1 to 3 ring structures were tested, and a plot of LC50 vs K_{OW} is shown in figure 4. A typical QSAR of increasing toxicity with increasing K_{OW} was evident for both animals.

All three compounds were more than an order of magnitude less toxic to both species than their PAH analogs (benzene, naphthalene, and anthracene). This is consistent with toxicity results obtained with midge larvae and green algae (Birge et al., 1985). A notable exception was the 3-ring acridine which was very toxic to *Artemia* while its PAH analog (anthracene) was completely non-toxic under the same specific test conditions.

Southworth et al., (1978) determined the bioconcentration and toxicity of 2, 3, and 4-ring azaarenes to *D. pulex*. They found that the bioconcentration factor and toxicity increased an order of magnitude with each ring addition, such that calculated lethal doses were relatively constant. Also uptake rates did not vary greatly between compounds, but the elimination rate decreased an order of magnitude with each ring addition. Thus the elimination rate appeared to be the most important kinetic factor regulating the bio-concentration of such compounds in *D. pulex*.

This and other data (Mackay and Hughes, 1985) support the hypothesis that bioconcentration and toxicity are due to a partitioning process regulated by the kinetics of uptake and release.

Chlorinate Methanes

Dichloromethane, trichloromethane, and chloroform were tested against both organisms and LC50's versus K_{OW} are shown in Figure 4.

As for the chlorobenzenes, acute toxicity and presumably bioconcentration increased with degree of chlorination in a predictable manner for both micro-crustaceans. Crisp et al. (1967) found essentialy the same progression in toxicity with reported EC50 values to *Elminius* (barnacle) larvae of 0.026, 0.016, and 0.035 fractions of saturated solutions in salt water.

Phototoxicity

When conducting tests with certain polynuclear aromatic hydrocarbons anomalous results have been obtained (by us and others) in that the chemical is much more toxic than expected. It can be hypothesised that a reaction product is responsible for the increased toxicity, the reaction being either enzymatic or photolytic. It has been observed that in the dark these hydrocarbons are non-toxic but in daylight or especially in UV light they become significantly more toxic. In our work anthracene has been used as a representative hydrocarbon to elucidate the nature of the phototoxic effect, how significant it is, and what the mechanism may be. Oil spills and industrial and municipal emissions of hydrocarbons will clearly have a much greater impact on the environment if natural sunlight can increase their toxicity.

The organisms used in the experiments were female *Daphnia magna* approximately 4-6 days old. A stock culture was maintained at 18-24 C under a 14L/10D photoperiod of flourescent light. The tests were conducted in filled, sealed 260 mL glass bottles. Ten animals were put in each bottle with 2 bottles per concentration and a control was always run. The tests were static and carried out at temperatures of 17-20 C. All anthracene solutions were made as dilutions of a 100% saturated solution. Parallel tests were always run in the ultra-violet light (24L/OD) and in the dark (OL/24D). When the *D. magna* were checked during the tests they were classified as follows: alive, moribund (lying on the bottom of the bottle with internal movement) and dead.

Two tests were conducted to determine if there is a phototoxic effect of anthracene on *D. magna*. Averaging the values, which were very close for both tests, the 24hr LC50 was a 16.3% saturated solution and the 48hr LC50 was a

12.5% saturated solution in the U.V. light. A 100% saturated solution is non-toxic in the dark. A similar test was done with *Artemia salina* and they also experienced a significant phototoxic effect, although they were less sensitive.

Tests were performed to determine if the photoproducts of anthracene were more toxic than the parent compound and would, therefore, be responsible for the increased mortality in the light. A 100% saturated anthracene solution was exposed to the U.V. light for 22 hrs and *D. magna* were then put in the undiluted solution. This solution of photoproducts was much less toxic in the light and, again, non-toxic in the dark. The *D. magna* were also exposed to a 100% saturated solution of anthraquinone, believed to be the dominant, stable photoproduct of anthracene. There was no mortality in the light nor in the dark after 48 hrs.

These tests show that anthracene is more toxic to *D. magna* after U.V. exposure but the products do not account for this increase in mortality. One mechanism proposed is that the animals take up the anthracene which is converted into a free radical or singlet oxygen by exposure to the U.V. light within the organism. This short-lived active species is responsible for the tissue damage and subsequent death.

A test was done to investigate the possible relationship between uptake time of anthracene prior to U.V. exposure and mortality. At least one hour of previous exposure to anthracene in the dark was needed to cause a significant increase in mortality.

Depuration tests were also conducted to determine if there is a connection between time allowed to excrete the anthracene before U.V. exposure and mortality. The *D. Magna* were put in a 100% saturated anthracene solution for 2 hours, removed and placed in clean water. They were left in the dark and then placed under the U.V. light at 30 min. time intervals. There was no significant death after 48 hrs.

Further work is being undertaken using depuration tests and water soluble free radical inhibitors in an attempt to elucidate this important phenomenon.

CONCLUSION

Several QSAR's have been presented for chlorinated methanes, benzenes, phenols, and biphenyls. In addition, the limits to its applicability for predicting biological effects have been shown through comparisons across chemical classes. Heterocyclic compounds were amenable to QSAR's for ring additions.

Inherent in all investigations was the assumption of a common toxic mechanism such that the toxic dose is constant and a 1:1 relationship exists between K_{OW} and the bioconcentration factor.

The work to date has demonstrated significant Quantitative Structure Activity Relationships (QSARs) which are consistent with the hypotheses. It is clear that the toxicity and bioconcentration potential of a homologous series of chemicals can be estimated, provided that data exist for some members. The QSARs can be used with some reliability for interpolation and with less reliability for extrapolation.

It is believed that such techniques could be invaluable for regulatory agencies because they could form the foundation of a system for rapidly estimating the toxicity of individual chemicals and mixtures. The model provides a rational method for estimating the toxicity of mixtures.

It is clear that in certain cases such QSARs may be misleading. Ionizing chemicals and those which photolyse rapidly require "custom" treatment. The use of QSARs must thus be coupled to a thorough understanding of the chemistry and biology of the systems being considered.

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Table 2: Selected physical-chemical properties and the acute toxicity of organic contaminants to *Daphnia*.

Compound	Fresh Water Solubility ($mmol\ m^{-3}$)	log K_{OW}	*Daphnia magna* 2d-LC50's	
			($mmol\ m^{-3}$)	(LC50/Cs)
Chlorobenzene	4.3×10^3	2.80	44.0	0.010
1,2 - CB	1.0×10^3	3.40	17.0	0.017
1,3 - CB	830	3.40	33.2	0.040
1,4 - CB	$C_S = 527^a$ $C_L = 1 \times 10^{3b}$	3.40	23.8	0.042
1,2,3 - CB	117 220	4.10	8.00	0.060
1,2,4 - CB	220	4.10	17.6	0.080
1,3,5 - CB	29 70	4.10	8.8	0.305
1,2,3,4 - CB	36 60	4.50	5.0	0.140
1,2,3,5 - CB	16.6 30.0	4.50	3.7	0.22
1,2,4,5 - CB	5.9 37.4	4.50	2.8	0.47
Penta - CB	2.6 10.0	5.00	1.72	0.66
Hexa - CB	1.7×10^{-2} 1.7	5.50	$>1.7 \times 10^{-2}$	>1.00
Biphenyl	48.6 138	3.90	9.4	0.19
O - PCB	26.5 36.7	4.3	4.8	0.180
m - PCB	14.0	4.6	1.1	0.077
p - PCB	6.2 21.0	4.5	0.87	0.14

4,4 - PCB	0.3 0.47	5.3	>0.3	>1.00
2,3,4 - CP	2532 11182	3.49	8.9	0.0035
2,4,5 - CP	4800 14967	3.72	12	0.0024
2,4,6 - CP	2195 6838	3.38	27	0.0123
2,3,4,5 - CP	434 4037	4.10	3.3	0.0076
2,3,5,6 - CP	431 4037	4.20	3.5	0.008
PCP	55.9 2958	4.60	1.20	0.025
Dichloromethane	228,000	1.51	5928	0.026
Trichloromethane	66,600	2.02	533	0.008
Carbon tetrachloride	5,340	2.79	182	0.034
Pyridine	n/a[c]	0.64	4994	—
Quinoline	464,540	2.04	1095	0.002
Acridine	46.8	3.40	14.5	0.31

a = actual solid solubility in water

b = theoretical sub-cooled liquid solubility

c = not available

Table 3: Selected physical-chemical properties and the acute toxicity of organic contaminants to *Artemia*.

Compound	Salt Water (30‰) Solubility (mmol m^{-3})	log K_{OW}	*Artemia* nauplii 2d - LC50	
			(mmol m^{-3})	(LC50/Cs)
Chlorobenzene	$C = 3.01 \times 10^3$	2.80	361	0.12
1,2 - CB	$C = 700$	3.40	105	0.15
1,3 - CB	$C = 581$	3.40	76	0.13
1,4 - CB	$C_S = 369^a$ $C_L = 700^b$	3.40	89	0.24
1,2,3 - CB	$C_S = 82$ $C_L = 154$	4.10	16	0.20
1,2,4 - CB	$C = 154$	4.10	18	0.12
1,3,5 - CB	$C_S = 20$ $C_L = 49$	4.10	5.2	0.26
1,2,3,4 - CB	$C_S = 25$ $C_L = 42$	4.50	5.0	0.20
1,2,3,5 - CB	$C_S = 12$ $C_L = 21$	4.50	7.4	0.62
1,2,4,5 - CB	$C_S = 4.1$ $C_L = 26$	4.50	>4.1	>1.00
Penta - CB	$C_S = 1.8$ $C_L = 7.0$	5.00	>1.8	>1.00
Hexa - CB	$C_S = 1.2 \times 10^{-2}$ $C_L = 1.2$	5.50	$>1.2 \times 10^{-2}$	>1.00
Biphenyl	$C_S - 34$ $C_L = 97$	3.90	19	0.57
o - PCB	$C_S = 19$ $C_L = 26$	4.3	7.8	0.41
m - PCB	$C = 9.8$	4.6	1.6	0.16
p - PCB	$C_S = 4.3$ $C_L = 15$	4.5	2.2	0.51

4,4 - CB	C_S = 0.2 C_L = 3.3	5.3	>0.2	>1.00
2,3,4 - CP	C_S = 1772 C_L = 7827	3.49	12	0.0068
2,4,5 - CP	C_S = 3360 C_L = 10477	3.72	28.9	0.0086
2,4,6 - CP	C_S = 1537 C_L = 4787	3.38	68	0.0440
2,3,4,5 - CP	C_S = 304 C_L = 2826	4.10	11	0.0360
2,3,5,6 - CP	C_S - 302 C_L = 2826	4.20	1.4	0.0047
PCP	C_S = 39 C_L = 2071	4.60	0.32	0.0081
Dichloromethane	160,000	1.51	6,080	0.038
Trichloromethane	46,600	2.02	1,445	0.031
Carbon tetrachloride	3,740	2.79	198	0.053
Pyridine	n/a[c]	0.64	15,171	--
Quinoline	325,178	2.04	859	0.0026
Acridine	32.8	3.40	1.41	0.043

a = actual solid solubility in water

b = theoretical sub-cooled liquid solubility

c = not available

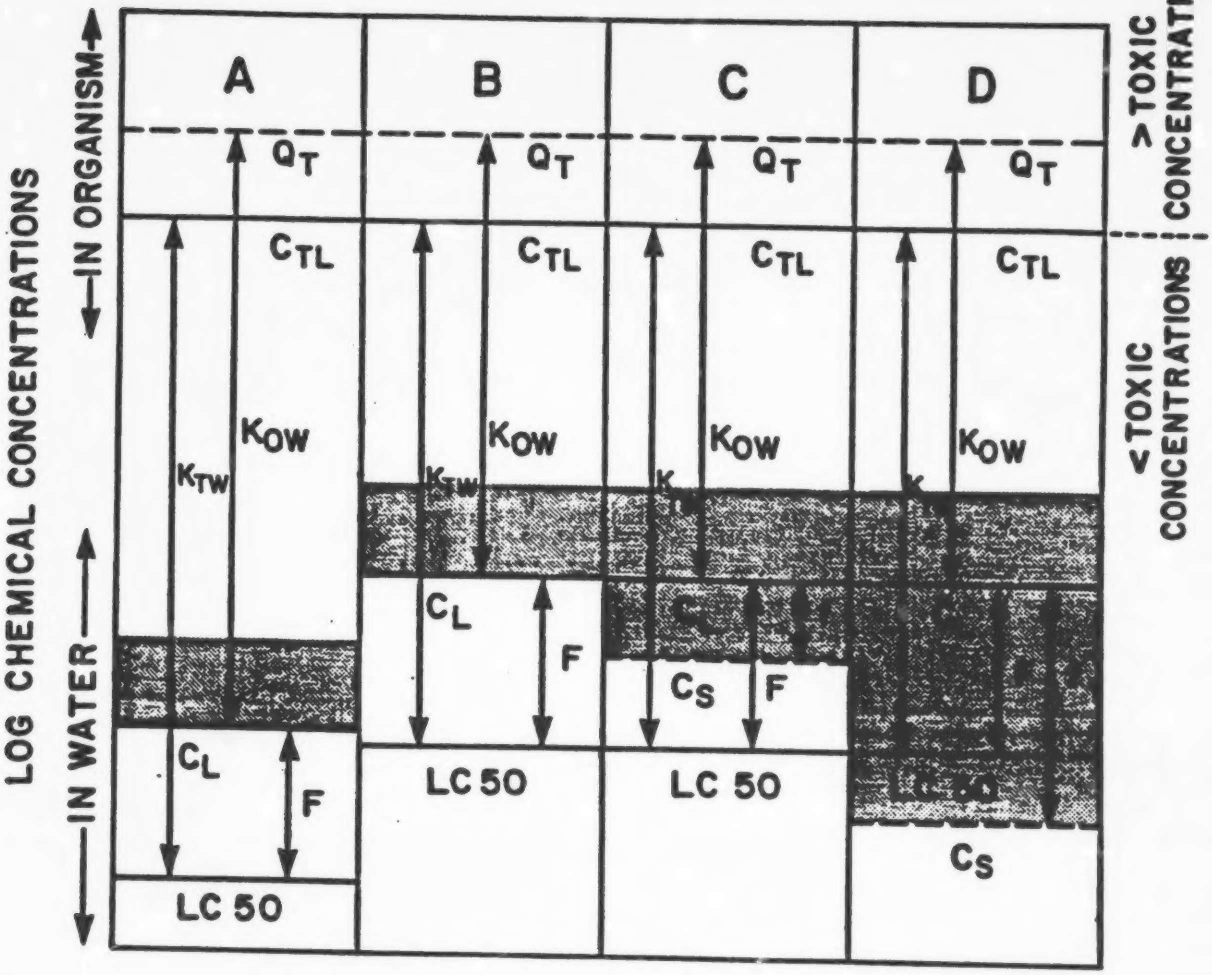
LOG CHEMICAL CONCENTRATIONS
IN WATER
IN ORGANISM
A
B
C
D
Q_T
C_{TL}
K_{TW}
K_{OW}
C_L
F
C_S
LC 50
>TOXIC CONCENTRATIONS
<TOXIC CONCENTRATIONS

Figure 1 : Diagram illustrating the relationships between water and organism concentrations,A for a low solubility,high Kow liquid,B for a more soluble lower Kow liquid,C for a solid of low melting point which can form a toxic solution in water, i.e. Cs>LC50 and D for a solid of high melting point which cannot form a toxic solution i.e. Cs<LC50. the lengths of the arrows are proportional to the concentration ratios. The hatched areas represent inaccessible super-saturated solutions.

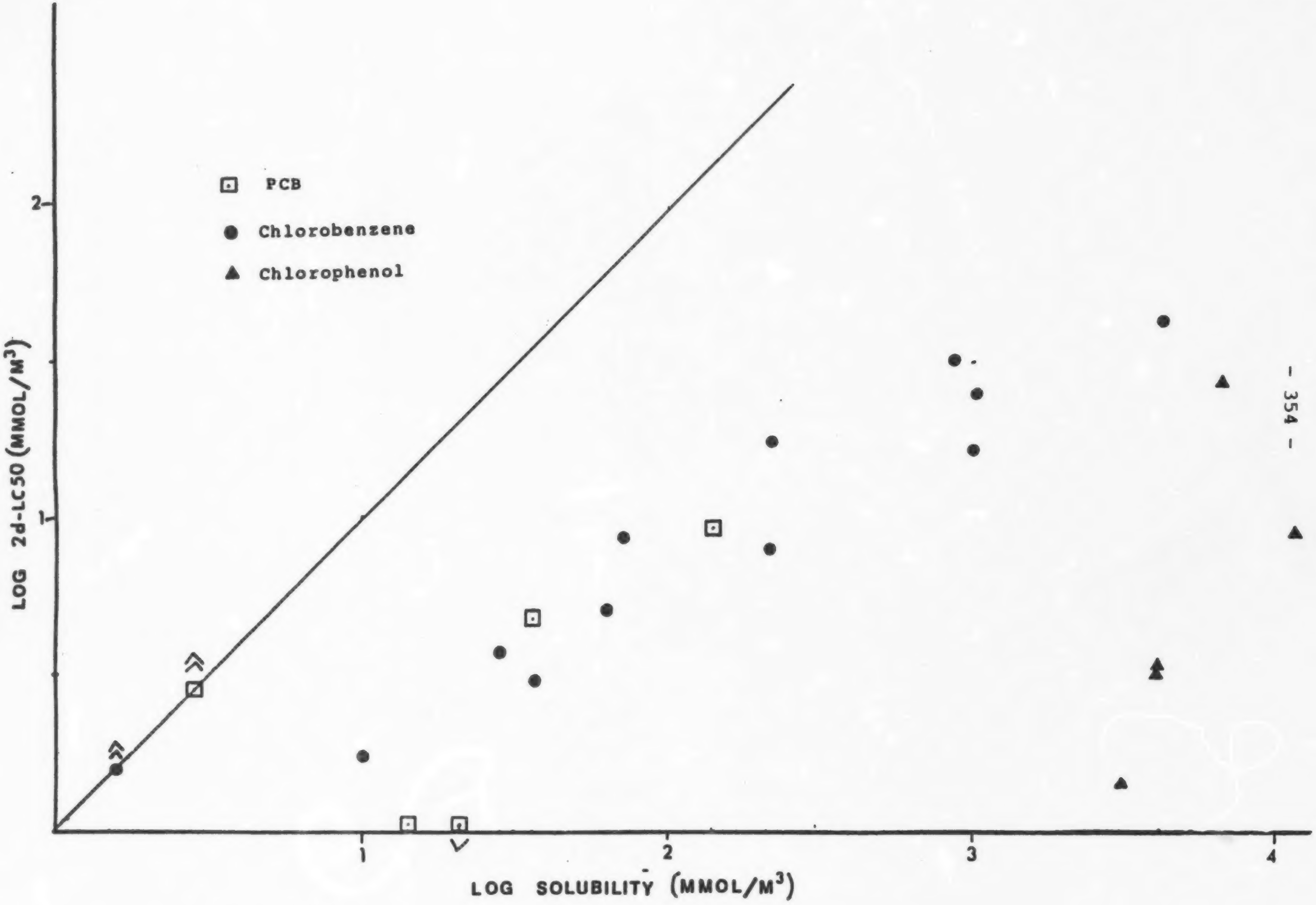

Fig. 2. The acute toxicity of chlorinated hydrocarbons to Daphnia magna as a function of solubility.

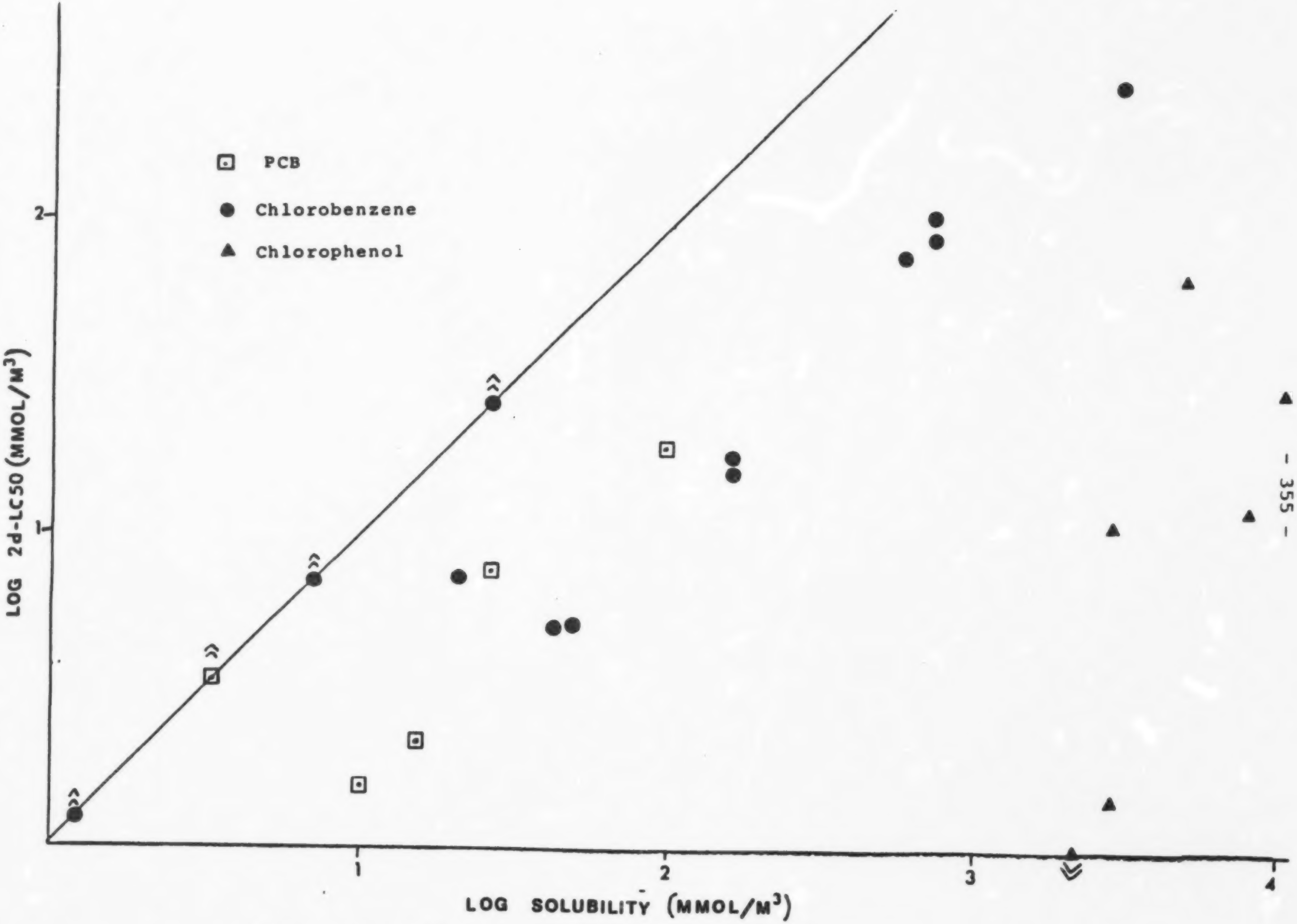

Fig. 3. The acute toxicity of chlorinated hydrocarbons to Artemia as a function of solubility.

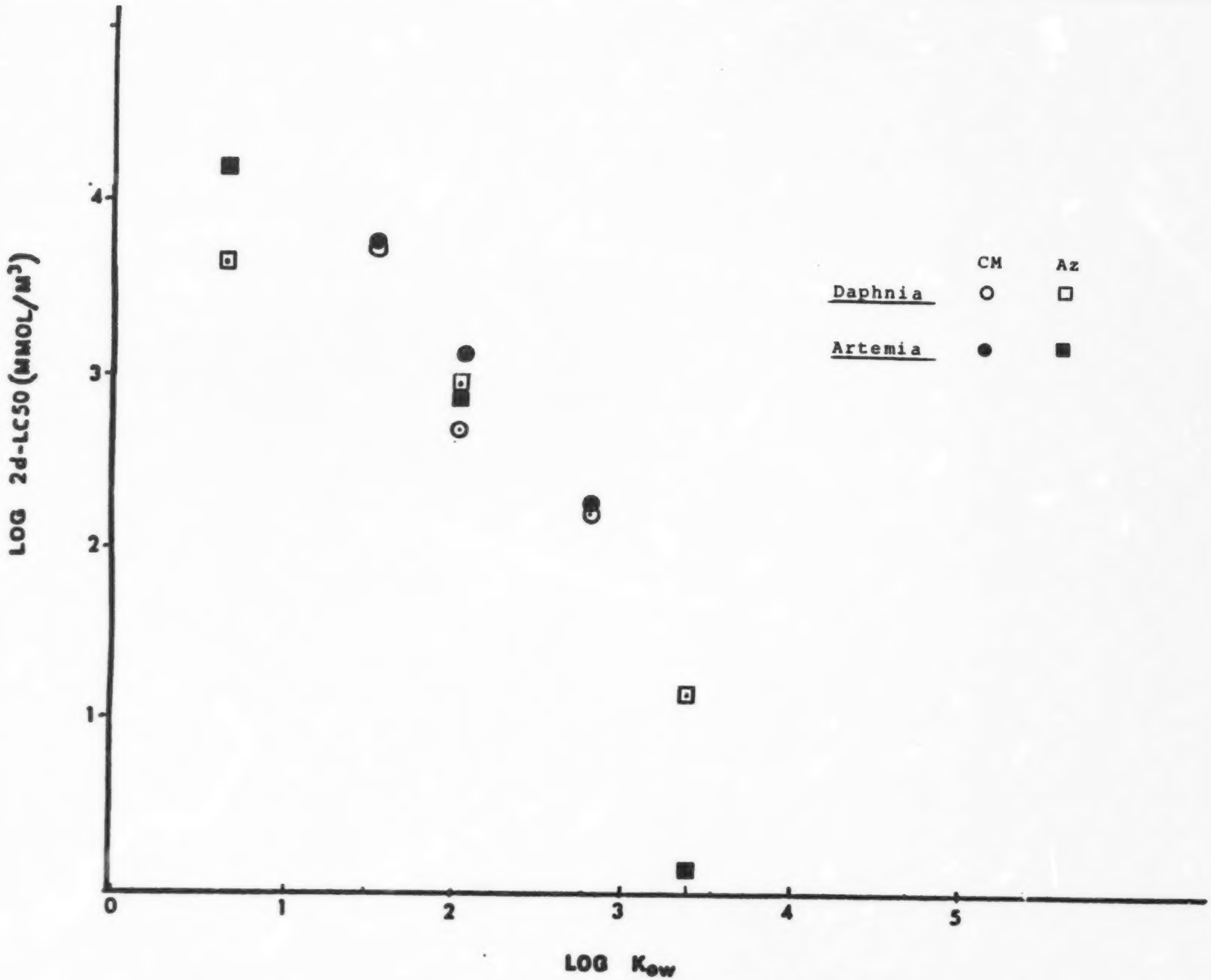

Fig. 4. The acute toxicity of chlorinated methanes and azaarenes to _Daphnia_ and _Artemia_ as a function of octanol/water partition coefficient.

THE SIGNIFICANCE OF NEOPLASIA IN FISH POPULATIONS

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Key words: Neoplasia, Fish, Fish Cancer.

ABSTRACT

Our primary goal is to undertake an initial review of environmentally associated cancers in wild fish populations, and to review the evidence that such neoplasms are causally linked to environmental pollutants. Specifically, we wish to determine the extent to which alternative genetic and infectious causes have been considered. We also plan to consider why many other species of fish exposed to the same polluted environment do not exhibit cancers to the extent seen in those affected fish which receive most investigative attention. Other goals are to characterize early precancerous tissue pathology in target species and to determine the biochemical basis of the high susceptibility to liver tumors in some fresh water fish.

Introduction

Many epidemiological surveys of naturally occurring neoplastic lesions in various fish in chemically polluted fresh water environments have provided circumstantial evidence that these lesions may be chemically induced by environmental pollutants (1-6). For example, in Lake Ontario, epidermal papillomas and hepatic or biliary neoplasms have been recognized in White Suckers and Brown Bullheads in polluted river waters (6). The association between neoplasms and pollution suggests a cause-effect relationship but presently there is insufficient epidemiological or laboratory evidence to unequivocally implicate pollution as a direct or indirect cause for any of these neoplasms. The apparent association between pollution and naturally occurring neoplasms may be sufficiently strong enough to suggest that these fish may be sentinels for environmental carcinogens potentially harmful to humans or other animal species that either inhabit the same environment or consume the affected fish (2-4). It is, therefore, important that the nature of any causative influences of environmental pollutants on naturally occurring fish cancers be well understood, so that any real and significant environmental risk factors can be appropriately managed and minimized.

However, the epidemiological and experimental studies required to firmly identify and evaluate a specific etiological factor involved in naturally occurring cancers are extremely complex and challenging. For example, the enormous research efforts that have attempted to define the role of aflatoxins in the multifactorial causation of human liver cancer (7) and the role of various dietary constituents in the causation of human gastric, colon and breast carcinomas (8) have yet to clearly identify and quantify causal roles for suspected agents. It is clear that most naturally occurring cancers are influenced by a multitude of factors that may influence the carcinogenic process in different ways at specific steps in the pathogenesis of these cancers. These cancers and their causative influences can best be understood by integrated multidisciplinary research that includes efforts that substantiate concepts relating to the biological effects of specific xenobiotic, dietary and viral agents, and, perhaps more importantly, concepts relating to the biological responses of tissues injured in various ways by these different agents (ie pathogenesis of biological alterations in affected tissues).

We are attempting to evaluate the pathogenesis of naturally occurring skin and liver neoplasms in wild Ontario fish on the premise that such an analysis will identify specific preneoplastic pathologic responses in affected tissues for which biological mechanisms can then be defined. By understanding these early tissue responses, we expect to be able to identify the types of basic tissue injuries that eventually lead to the neoplasms observed at the end stage. This identification of basic tissue responses will in turn lead to an understanding of the types of agents (eg. viral, parasitic, chemical, nutritional, etc.) that are the most likely causes of the basic responses involved in carcinogenesis, including phenotypic cellular alterations, mitoinhibition, lethal injury and growth stimulation.

By this approach, our analysis of the actual disease problem is not focused specifically on any one of various putative causative agents. This approach utilizes established expertise in interpreting the pathogenetic responses of fish tissues to numerous agents of disease (6) and also borrows heavily from work on the sequential biology of preneoplastic and neoplastic responses of mammalian tissues during naturally occurring and chemically induced carcinogenesis (9-10). The objective of this presentation is to delineate some aspects of the biology of tissue responses likely to be relevant to the mechanistic analysis of the major naturally occurring neoplasms that are currently of concern in some Lake Ontario fish.

Agents versus Responses

A major axiom in the study of chemicals as carcinogens is that specific chemicals can be categorized as noncarcinogens or carcinogens of various types and potencies according to their chemical properties. For example, a chemical might be termed genotoxic and a potential initiator of carcinogenesis, based on its ability to covalently interact with or otherwise induce "permanent" genetic alterations in some cells with a resulting increased likelihood of progressing to cancer (11). Also chemicals may be designated as promoters if they accelerate, by various means, the progression of "initiated" cells towards cancer (10-11). The attractiveness of this approach lies in the potential to "weight" a specific agent with respect to its carcinogenic potential and thereby to implement strategies designed to minimize carcinogenic risks associated with exposure to it. However, the carcinogenic process involves many different tissue responses which will be discussed in the next section. These responses may be influenced in different and frequently opposite directions by a given agent, such that the carcinogenicity of an agent depends at least as much on the circumstances of exposure as it does on the chemical characteristics of the agent (9).

Polychlorinated biphenyls (PCB) are a good example with which to illustrate this point. The concerns that PCBs are carcinogenic are largely due to the recognition that (1) PCBs enhance the mutagenicity of other xenobiotics by inducing (increasing) various cytochrome P-450 species that activate xenobiotics to metabolites that interact with DNA (12) and (2) PCBs at high and prolonged dosages stimulate (promote) the emergence of phenotypically altered liver cells which are previously initiated by other carcinogens, or which are generated spontaneously with age in rodents (13,14). However, PCBs at low levels usually reduce the initiating potency of carcinogens _in vivo_ (15) and also abrogate the promoting effect of toxic liver carcinogens such as aflatoxin B_1, 2-acetylaminofluorene (2-AAF), azo dyes and nitrosamines (16,17). These latter anticarcinogenic effects are attributable to the many detoxification enzyme systems induced by low levels of PCBs (12) and these more than compensate for any induction of cytochrome P-450 dependent activation systems (16).

The evidence for carcinogenicity of PCBs is obtained from operationally contrived models in which either these detoxification systems are suboptimal (ie Salmonella/microsome mutagenicity assays), or the exposure to initiating carcinogen and PCB is sequential rather than concurrent. The evidence for anticarcinogenicity of PCBs, on the other hand, is obtained from models in which the complete PCB-induced phenotype coincides with the exposure to known carcinogens, and as such, more realistically resembles natural exposure to PCBs in combination with many other agents. These studies, and other work that demonstrates that PCBs themselves do not initiate carcingenesis (18) indicate that it is not reasonable to designate PCBs as carcinogens on the basis of selected evidence, because they are more likely to be anticarcinogenic under natural low level continuous exposure conditions. This assessment is consistent with the lack of hard epidemiological evidence implicating PCBs in naturally occurring neoplastic diseases of man and animals. These various studies further illustrate the point that the potential role of PCBs or similar xenobiotics in carcinogenesis can be better understood from analysis of their influences on all specific tissue responses involved in carcinogenesis than from selected effects of xenobiotics such as mutagenicity, genotoxicity or monooxygenase induction.

Tissue Responses Involved in Carcinogenesis

Many studies with chemically induced liver and skin cancers in experimental mammalian models (9,10,19) have elucidated a number of critical biological steps. These steps are considered relevant to the prolonged sequence of cancer development in these and other tissues exposed to various oncogenic factors including radiation, chemicals, viruses, parasites, nutritional perturbations and genetic anomalies. Many of these steps have been characterized mechanistically, and can be recognized during the carcinogenic process by specific tissue responses to agent-induced injuries (9). A first step is initiation which is recognizable by the appearance of phenotypically altered cells. These cells are generated under conditions that involve a primary DNA injury, usually covalent chemical modification, which subsequently results in fixation of a change in gene expression if cells are stimulated to proliferate before the DNA damage is fully repaired (9,19). Many genotoxic carcinogens such as nitrosamines and polyaromatic hydrocarbons are good initiators of liver carcinogenesis because they are activated to metabolites that alkylate DNA without substantially affecting the ability of cells to proliferate (19). However, many other carcinogens such as aflatoxins, pyrrolizidine alkaloids, azo dyes and aromatic amines also alkylate DNA extensively but are weak initiators because they also inhibit cell proliferation (20). Under these conditions, DNA repair may procede to completion before proliferation.

Cell proliferation is a tissue response essential for initiation (and also promotion and progression as discussed below) and may result from regeneration after necrosis, developmental growth, maintenance growth or induced (hyperplastic) growth (9,19,20). These multiple requirements for cell proliferation during various steps in carcinogenesis explains the predisposition to cancer development in tissues with a high cell turnover rate or that are rapidly growing, regenerating after injury or stimulated by viruses or hormones or xenobiotics. As such, the cell proliferative responses of different types, which can be recognized by pathologic evaluation, reflect a carcinogenic predisposition in a tissue and also reflect the nature of various potential insults that can elicit the various proliferative responses.

Phenotypically altered cells can be identified by appropriate markers (eg. enzyme activities, etc.) and by morphological appearance (19). They, or the small subpopulations (clones) of their progeny cells can be quantified and this then is an index of the extent of initiation by genotoxic agents. In experimental liver cancer models, these initiated populations can be identified by any or all of a wide spectrum of enzymes involved in xenobiotic activation (decreased) or detoxification (increased). Most frequently, γ-glutamyltranspeptidase and isoenzymes of glutathione-S transferases, all of which are involved in excretion of glutathione conjugates of xenobiotics, are used as markers (9,19,20,21).

The generation of phenotypic variants during initiation is by no means a harmful response. In fact, such cells are frequently generated in large numbers in many tissues over the lifespan of the host (10), and these cells frequently act as a reserve of cells better equipped to restore functional tissue mass in the face of severe insults such as chemically induced necrosis or mitotic inhibition (9). Because many of these altered cells can reacquire a normal phenotype, the process of initiation has been considered an adaptive response to tissue insults (9).

However, when these latter insults are protracted, some of these cells will give rise to persistent enlarged populations (nodules or papillomas) in which additional permanent changes may occur. The process by which altered cells are selectively stimulated into nodules and papillomas is termed promotion, and this process may be elicited by several distinct tissue responses including selective killing (eg. dietary deficiencies, toxic agents) or inhibition of unaltered cells, (eg. viruses, toxic chemicals). In various chemical, nutritional and viral experimental models of skin, liver, urinary bladder and colon carcinogenesis, the promotion step is reversible because altered populations disappear when the selective stimulus for their proliferation subsides (9,10). However, because a small proportion of these altered populations may acquire permanent changes, any promoting influence can enhance carcinogenesis. The persistently proliferating populations eventually give rise to diversified subpopulations of new cells, some of which may have aggressive properties such as expansive growth, invasive growth or metastasis (9,19). These latter responses are readily recognized in the late phases of cancer progression but, since they cannot yet be explained mechanistically, usually do not give much indication as to the types of insults involved in this late stage. However, there is some evidence to indicate that initiating and various promoting xenobiotics have little influence on these later stages, particularly since, in the liver at least, these populations are highly resistant to further chemical injury by virtue of their altered resistant phenotype.

The following is a specific example in chemical hepatocarcinogenesis that illustrates how the responses to chemical injury explain, in mechanistic terms, the carcinogenic potential of a toxic substance. Aflatoxin B_1, 2-AAF and pyrrolizidine alkaloids are strongly genotoxic agents but very weak initiators because they inhibit hepatocyte regeneration (20,21). This latter response, however, does enhance the selective proliferation of very small numbers of altered cells that are resistant to these chemicals (21). As such, these genotoxic agents are potent carcinogens, not so much because of their ability to alkylate DNA, but because they are extremely potent promoters by virtue of their mitoinhibitory and cytocidal toxic effects. Hepatocarcinogenic insults of this type can be recognized by the tissue response patterns induced, including hepatic atrophy, bile duct proliferation and resistant nodular proliferation (19,21). It is important to recognize that for these agents at least, the carcinogenic potential is mostly due to general toxic effects of relatively high levels of chemical affecting the entire tissue mass. By comparison, the initiating activity can be attributed to genotoxic effects of lower dosages that affect only a very small proportion of cells that are unlikely to progress in the absence of the promoting influence.

Biological analysis of naturally occurring preneoplastic and neoplastic responses in fish

On the basis of the foregoing concepts of how cancers develop in response to various agents, we anticipate that the naturally occurring problems of skin papillomas and hepatic neoplasms in wild fish can be mechanistically analysed in the following manner. Tissue responses in the target tissue should exhibit evidence for (a) agent exposure (b) phenotypic cellular alterations (ie. initiation), and (c) increased proliferative stimulation, either hyperplastic or regenerative. By recognizing and quantifying each of these component responses in affected fish during the early stages of tumor development, it should be possible to deduce the nature and severity of the various primary tissue insults and thereby predict the likely agents involved at specific stages in the carcinogenic process. The following outline illustrates how this can be achieved.

Evidence for agent exposure

Many environmental xenobiotics, viruses and parasites can be directly detected in tisssues of wild fish. While this is clear evidence of exposure, it does not necessarily indicate that such exposures perturb tissue functions. Perturbation must be detected by alterations in tissue form or function. For example, exposure to some xenobiotics results in adaptive physiological responses including induction of various mixed function monooxygenases (ie. cytochromes P-450) or induction of phase II detoxification systems. Most surveys for this evidence of chemical exposure have focused on mixed function oxygenases (5) but few have examined phase II enzyme systems (22). Since the latter tend to be less specific for particular xenobiotics (12), more readily determined in samples collected from field sources, and markedly increased in preneoplastic lesions (9), we have developed methods that detect glutathione-S-tranferases, glutathione reductase, glutathione peroxidase, γ-gluthamyl transpeptidase and UDP-glucuronyl transferases in fish livers from field sources. While there is presently only limited evidence that these enzymes are induced in skin of mammals exposed to topical xenobiotics, we expect that these enzyme functions will also be increased in skin of fish exposed to xenobiotics such as PCBs.

While induced alterations of these enzymes may indicate xenobiotic exposure and response, they do not necessarily indicate harmful perturbations likely to increase cancer initiation or progression. Direct evidence for harmful perturbation include toxic cell injures such as degenerations and inhibition of proliferation. These responses can be recognized by direct morphological examinations of target tissues from evidence such as apoptosis, necrosis, reduced tissue mass and secondary inflammatory and repair responses. The location and extent of these various responses, especially if observed in the presence of a chemical or biological agent (eg. parasite, virus) will give evidence that the target tissues are harmfully perturbed by exogenous potentially carcinogenic agents.

Evidence for phenotypic alterations of target cells

The most direct evidence that agent exposures initiate the carcinogenic process comes from the clear identification of early phenotypically altered populations of cells in target tissues. While these altered cells can be provisionally identified by various histopathologic criteria, unequivocal evidence requires the demonstration of appropriate tissue markers. By extrapolating from a large body of established data for mammalian liver cell alterations (9), we are developing histochemical and immunocytochemical methods for detecting increases in glutathione-S-transferases in skin, liver and bile duct cells of affected fish. By preparing specific antibodies to purified glutathione-S-transferases, it should be possible to survey a large collection of formalin fixed tissue blocks for populations of cells with increases in these enzymes. This approach has the advantages that samples from field sources can be readily processed by routine formalin fixation, and evaluated by quantitative morphometry for the rates of initiation in target tissues of the respective species at relatively young ages. Such an approach has already been successfully implemented for rat liver carcinogenesis.

Evidence for increased proliferative stimulation

Proliferative responses in target tissues are readily recognizable by histological criteria in routine hematoxylin and eosin stained tissue sections. Of particular importance is the determination of the nature of the proliferative response. For example, proliferation due to agents such as PCBs and various hormones that induce hyperplasia and hypertrophy can be regarded as surplus growth and thus occurs in tissues that are increased in size without evidence of post necrotic regenerative (repair) proliferation. By comparison regenerative proliferation usually occurs in a tissue that has previously undergone a reduction in functional tissue mass (ie. necrosis). Each of these proliferative responses is diffuse within the extent of agent-induced injury. Other types of proliferative responses also can be recognized including metaplasia and compensatory hyperplasia of some cells refractory to destructive injury or mitoinhibitory insult (eg. bile duct proliferation in atrophic livers). Clonal proliferation in altered nodules and papillomas reflects a combination of initiation and any of the various types of proliferative stimuli described above. While any proliferative stimulus has the potential to initiate and promote such lesions towards cancers, their different biological mechanisms reflect different primary perturbations in the target tisssues.

Conclusion

This strategy has the advantage of defining the extent and nature of specific tissue insults that occur early and possibly intermittently in the sequence leading to cancer. This approach ignores an important aspect of the process, namely the later steps involved in transformation, oncogene expression and diversification during progression into aggressive neoplasms. Presently, technology and concepts relating to how exogenous agents may influence these later steps are not sufficiently developed to enable the analysis we think can be achieved with studies on the early responses. Also, the late responses are relatively rare and usually occur in the absence of residual evidence for the earlier insults. However, the early responses while not necessarily committed to cancer development will enable a clearer understanding of the chronology and epidemiology of causative insults in a larger and younger population of affected fish.

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EPIDEMIOLOGICAL STUDY OF DISEASE INCIDENCE AND RECREATIONAL WATER QUALITY AT SELECTED CONSERVATION AREAS IN SOUTHERN ONTARIO

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Key words: Epidemiology, Water Quality, Bacterial Pollution, Ontario Beaches.

ABSTRACT

Results of two separate prospective epidemiological surveys at Ontario beaches have shown that morbidity rates are higher among swimmers than among non-swimmers. Swimmers have been shown to experience respiratory ailments most frequently followed by gastrointestinal, eye, ear, skin, and allergenic symptoms.

Concomitant with the epidemiological surveys, water samples were collected at the beaches and analyzed for total staphylococci, heterotrophic plate count, fecal coliforms, *Escherichia coli*, fecal streptococci, enterococci and *Pseudomonas aeruginosa*. In all investigations of this nature carried out thus far, correlations between bacterial levels and incidence of illness among swimmers and non-swimmers have been calculated for single organisms only. For example, on our first survey, morbidity among swimmers was shown to be related to staphylococcal counts ($p < 0.001$), to fecal coliform levels ($p < 0.001$) and to fecal streptococcal counts ($p < 0.016$). In this study, combinations of organisms such as *E. coli*, total staphylococci, and *P. aeruginosa* will be incorporated into the multiple regression analysis in various mathematical combinations, to determine if multiple indicators will be more appropriate as water quality parameters. Computer analyses are currently being carried out on the data.

INTRODUCTION

In a previous report (1), preliminary results from an epidemiological study of swimming-related illness and recreational water quality in Southern Ontario were presented. The objectives of this paper are: 1) to outline, quantitatively, the relationship between bacterial water quality and swimming-related illness, and 2) to evaluate current bacteriological guidelines for bathing water quality in the Province of Ontario.

Whether or not bacteriological guidelines are necessary for recreational waters has been a controversial issue for over twenty-five years (2,3). In Ontario, Canada, the existent guideline for fecal coliforms, the present North American indicator of choice, is a geometric mean density of 100 fecal coliform bacteria per 100 mL of water. For most other Canadian provinces and several American states, the limit is a geometric mean density of 200 fecal coliforms per 100 mL of water (4,5). Existing guidelines are presented in Table 1 (6).

Of issue, at present, is an intensive review of the merits of several bacterial water quality indicators, as well as the determination of acceptable bacterial levels from the public health viewpoint. In order to address these issues, a prospective epidemiological investigation was conducted at six Southern Ontario beaches during the summer of 1983.

METHODS

Beach Sites

Beaches were selected for study (Figure 1) at the following locations: Albion, Boyd, Claireville, Heart Lake, and Kelso Conservation Areas, as well as a beach at Professor's Lake.

Bacteriological Survey

Surface water samples were collected, in sterile bottles, at a lake depth of 50cm in an area with a maximum density of swimmers. At the time of sampling, air and water temperatures were recorded, as well as a brief weather description. The turbidity of the water and whether the lake was wavy or calm were noted. Counts of the number of persons on the beach who were not swimming were estimated. For those persons in the water, the number of persons with their head underwater was estimated. Unless the beaches were closed for swimming, water samples were collected twice daily on weekends. Closed beaches were usually sampled once daily. A record of the sampling dates and beach status (open or closed) is listed in Table 2. The samples were chilled on ice during transport to the laboratory and processed within six hours.

Surface water samples were analyzed for: total staphylococci, heterotrophs, fecal coliforms, _Escherichia coli_, fecal streptococci, enterococci, _Pseudomonas aeruginosa_, _Campylobacter jejuni_, and _Legionella_ sp.

For the enumeration of total staphylococci, surface water samples were filtered through 0.45 μm Gelman filters and incubated for 24 to 48h at 35°C on Vogel-Johnson agar (Difco) supplemented with 0.5% sodium pyruvate (R. Alico, personal communication). Aerobic heterotrophic bacteria were isolated on Casein-Peptone-Starch agar plates (7) which were incubated at 20°C for seven days. Fecal coliforms and E. coli were enumerated by filtering appropriate volumes of each sample and placing the filter on mTEC (medium for thermotolerant E. coli) media. The plates were placed in plastic cakettes, with two ice jars in each, and incubated at 44.5°C (8). Fecal coliform counts were performed after 20 +/- 2h. The filters were then transferred to pads, saturated with urea for a 15 minute period and yellow colonies were verified as E. coli by oxidase and urease activities, and growth on citrate agar (Difco) (9).

A membrane filter technique employing m-Enterococcus (mE) agar (Difco) was utilized to quantitate fecal streptococci (10). Membrane filtration was also used to isolate enterococci (11). Filters were placed onto mE plates and incubated for 48h at 41°C. Following incubation, the membrane was transferred to an Esculin-iron agar plate. After 20-30 min at 41°C, small black spots appeared under positive colonies. To verify the colonies, the bile-esculin medium of Schwan (11) was used along with: 1) growth at 45°C in BHI (Brain Heart Infusion) broth, 2) a negative catalase test, 3) growth on 40% bile-blood agar, 4) a positive Gram stain, 5) acid reaction in litmus milk, and 6) esculin hydrolysis (11).

Pseudomonas aeruginosa were enumerated by membrane filtration using two different media for comparative purposes. The filters were placed onto plates of a Ministry of the Environment modification of the mPA medium (Appendix) and also onto mTIN medium, a new medium developed by our laboratory (in preparation). The plates were incubated at 41.5°C for a minimum of 48h.

For isolation of Campylobacter jejuni, water was filtered and the filters were added to BNP broth (modified Brucelia broth, Appendix) for enrichment. Flasks of broth containing the filters were incubated under microaerophilic conditions (air was evacuated from an anaerobic jar and replaced with a mixture of N_2, O_2, and CO_2) at 42°C for 48h. The enriched culture was streaked onto Skirrow´s agar (12), and the plates were incubated at 42°C for 48h, under the same atmospheric conditions as described above.

The procedure employed for the isolation and enumeration of Legionella pneumophila from water was developed by the Canada Centre for Inland Waters (Appendix).

Epidemiological Survey

A total of 9,296 people were interviewed on weekends, in order to obtain maximum numbers of beach participants. Interviewers were uniformly trained and monitored carefully. Family units were preferentially selected for interview in order to facilitate accurate and accessible follow-up information. Beach groups of size six or less were considered ideal. During the initial interview, a contact or spokesperson was appointed for each beach group. Information collected from each beach group member included: relationship to the contact person, age, sex, previous swim record for the past four days, whether the person swam or would swim on the interview day, whether the head was immersed in the water, previous and current illness record for the past four days, and the best time of day to telephone the contact person. This information was recorded on the "Initial Interview Form" (Appendix).

For the follow-up information, an interviewer telephoned the contact person within seven to ten days of the initial interview. The interviewer obtained answers to the questions listed on the "Telephone Follow-up Form" (Appendix) and recorded the date when any symptoms were first noticed. The telephone questionnaire attempted to determine whether illness occurred within three days (for reliable information, exclusion of illnesses with long term incubation periods, and to attempt to avoid peron-to-person transmission of disease within a household, as well as to avoid the problem of excessive numbers of potential confounding variables) subsequent to swimming at a specified location. The questionnaire also assessed: the symptoms of the illness, whether medical attention was sought and the physician´s diagnosis, whether the disability resulted in staying home from work and the duration of the period spent at home, and confirmation of the water exposure data. People who swam in alternate or the same locations within four days prior to, or three days subsequent to, a trial were analyzed by instituting a separate variable in the analysis.

Statistical Analysis - Bacteriology

Geometric means of the bacterial counts were calculated by computer using the method recommended by the Ontario Ministry of the Environment (L. Vlassoff, personal communication), that is:

$$\text{geometric mean}=\exp \{((\ln x_1+\ln x_2+\ldots+\ln x_n)/n)\}.$$

Overall geometric means of bacterial counts were calculated based upon the total number of samples collected. For epidemiological purposes, however, bacterial geometric means were calculated daily (ie: by beach, month, and date, collectively) since the associated epidemiological illness rate was ascertained daily.

In order to test whether bacterial counts for a specific organism were significantly different between open and closed beaches (ie: by status), between beaches (ie: by beach), between open and closed beaches (ie: by beach and status), and between months (ie: by month), the ANOVA (analysis of variance) computer procedure in SAS (Statistical Analysis System) was used (13). Specifically, the LSD (Fisher´s Least Significant Difference) multiple comparison test was employed in the ANOVA procedure. Significance testing of geometric means, directly, is not available, thus, natural logarithm ($\log_e$ or ln) values of the raw bacterial counts were used for comparison testing by the LSD procedure. This is an equivalent to the above direct test.

Statistical Analysis - Epidemiological Regression Modelling for the Prediction of Illness

The FUNCAT procedure, in SAS, was utilized to generate predictive illness models (14). FUNCAT models FUNctions of CATegorical responses by linear logistic regression (14). It uses the maximum likelihood method to aid in selecting the most appropriate model, and provides parameter estimates, as well as approximate chi-square test statistics to determine the relative importance of the factors in the model (15). FUNCAT, then, was used for linear logistic regression modelling so that the effects of confounding variables could be analyzed along with the bacterial counts. A particular illness (the outcome) and the bacterial count (one independent variable) were always included in the model, as well as other independent variables which significantly assisted in explaining the variation in response. A FUNCAT predictive model may be written in this way:

$$\text{logit } p=\ln(p/1-p)a+B_1x_1+B_2x_2+B_3x_3+B_4x_4 \quad (16),$$

where p is ill, 1-p is not ill, a is the intercept or mean of the illness rate, x_1 is age (a continuous variable), x_2 is contact person (a discrete variable), x_3 is interviewer, x_4 is $\log_{10}$ of the geometric mean of the particular bacterial count, and the B´s are the coefficients of the terms in the model.

In choosing a particular model, all important factors were entered into the model, and then factors with a chi-square p value greater than 0.05 (the 5% level) were dropped, one at a time, in order from the largest to the smallest p value. For each step, if the rounded iteration 0 loglikelihood minus the rounded final iteration loglikelihood (for the larger model subtracted from the smaller one) yielded a value which is significant at the 5% level (when one considers the degrees of freedom, by subtraction) the factor was kept in the model. The resultant predictive model, which can be used to predict illness occurrence, evolved from the observed data and provided predictive parameter estimates. If these estimates were positive in sign, the particular category of the factor contributed to the probability of illness, if all other factors were held fixed.

Predictive logistic regression models were determined for: swimmers, waders, and persons who did not enter the water, collectively. However, it was decided to concentrate upon models for swimmers only, due to their large numbers and thus more reliable relationships, and for the purpose of graphic illustrations versus bacterial count. The four best models, based upon the chi-square p values for bacterial count, were graphed.

In order to graphically depict the predicted relationship between illness in swimmers and bacterial count, a subseqent additional linear logistic model was fitted using the observed logits ($\log_e$ (p/1-p), probability of illness) as the dependent variable, and the $\log_{10}$ of the geometric mean of the bacterial count as the independent variable, forcing the slope associated with the latter variable to be that obtained from the original full predictive FUNCAT model (that model which included all the important confounders). This was done using the GLIM system (17,18). This procedure was developed for graphic and visual presentation. Thus, the coefficient of the $\log_{10}$ of the geometric mean of the bacterial count was used as the slope for the graph.

Finally, some FUNCAT predictive regression models were developed to test the effectiveness of existing Ontario and American recreational water quality guidelines.

RESULTS

1) Microbiology

The overall bacterial geometric mean data are presented in Table 3 and Figure 2. Statistical tests (only those comparisons significantly different at the 5% level are listed in Tables 3,5,7, and 8) of the natural logarithms of the bacterial counts, by status (ie: open versus closed beaches) appear in Table 4. By the LSD test, significantly different comparisons at the 5% level were evident for only the total staphylococci and the enterococci. In general, then, there was no significant difference between open and closed beaches.

In Table 5, the geometric means of the bacterial counts are depicted by month and the associated statistical tests of the natural logarithms of the bacterial counts appear in Table 6. Statistically significant differences were detected between June and July for heterotrophs and the enterococci, between July and August for total staphylococci, heterotrophs, E. coli, fecal coliforms, and fecal streptococci, and between June and August for total staphylococci, heterotrophs, the enterococci, and fecal streptococci. No significant differences were found for P. aeruginosa on mPa or mTIN.

The geometric means of the bacterial counts are presented by beach and by beach and status in Table 7 and Figures 3 and 4. Statistical testing of the natural logarithms of the bacterial counts is presented by beach in Table 8, and by beach and status in Table 9. Several significantly different comparisons arise in these data. With regard to beach, the maximum significantly different comparisons were observed between Boyd Conservation Area and Professor´s Lake, and between Kelso Conservation Area and Professor´s Lake.

2) Epidemiology

A very good response rate of 90% was achieved in the epidemiological survey (Table 10).

Crude symptom rates for the study population used in regression modelling (ie: those persons for whom no missing values were present for the factors considered) are listed in Table 11 and Figure 5. Significant differences at the 5% level or better were detected between persons who entered the water and those who did not, and between swimmers, waders, and persons who did not enter the water for all categories of morbidity other than the allergy category. The overall trend of greater morbidity in swimmers versus waders versus persons who did not go into the water is quite apparent and intriguing. Many factors, including the bacteriological quality of the water, may explain this trend.

3) Logistic Regression Modelling - For Swimmers Only

Let us now consider the results depicted in Figures 6 to 9 and Tables 12 to 15. The first three models represent the best models of those tested for particular illness categories in swimmers and the final model was the best model for overall illness, collectively, in swimmers. For gastrointestinal illness, E. coli, fecal coliforms, fecal streptococci, and the enterococci were all tested. For skin, eye, and respiratory problems, total staphylococci were tested. For ear problems, P. aeruginosa on mPA and mTIN were analyzed. If one examines the effects of the factors in the respective models (Tables 12 to 15), the order for the best to worst p value associated with the particular chi-square value of the bacterial count (specifically, $\log_{10}$ of the geometric mean of the bacterial count) was: 0.0881 for fecal coliforms (in the fecal coliform-gastrointestinal illness model), 0.0947 for total staphylococci (in the total staphylococci-skin illness model), 0.1021 for E. coli (in the E. coli-gastrointestinal illness model), and 0.1237 for P. aeruginosa (on mPa, in the P. aeruginosa - overall illness model). Since all of these values were greater than 0.05 for the $\log_{10}$ of the geometric mean of the bacterial count, we have no evidence that the count contributed to the prediction of illness in swimmers. In Figures 6 to 9, the order from the best to worst slope was: 0.560 for total staphylococci, 0.347 for fecal coliforms, 0.325 for E. coli, and 0.182 for P. aeruginosa. These results suggest that, although as the geometric mean of the bacterial count increased, illness also increased, but this was not significant (as indicated by the chi-square p valuefor the $\log_{10}$ of the geometric mean count in the model), and thus no dramatic slopes were evident.

In Figure 6, the graphic representation of the logistic regression model results for fecal coliforms versus gastrointestinal illness is shown. At a geometric mean bacterial count of 100, approximately 1.5% (+/-2 x 0.2) of the swimmers would be expected to become ill. The same values at geometric means of 200, 500, and 1,000, respectively, would be approximately: 1.8%, 2%, and 2.4%. The observed rate of gastrointestinal illness in persons who did not enter the water was 0.50%, if one uses the same population as that used in modelling. The factors which significantly altered the model are listed in Table 12. They were: age and interviewer (p=0.0001), and contact person (p=0.0141).

In Figure 7, the graphic representation of the logistic regression model results for E. coli versus gastrointestinal illness is portrayed. At a geometric mean bacterial count of 100, approximately 1.8% (+/-2 x 0.2) of the swimmers would be expected to become ill. The same values at geometric means of 200, 500, and 1,000, respectively, would be approximately: 1.9%, 2%, and 2.5%. The observed rate of gastrointestinal illness in persons who did not enter the water was 0.50%, if one uses the population used in modelling. The factors which significantly altered the model appear in Table 13. They were: age and interviewer (p=0.0001), and contact person (p=0.0141).

In Figure 8, the graphic representation of the logistic regression model results for the total staphylococci versus skin illness is shown. At a geometric mean bacterial count of 100, approximately 0.7% (+/-2 x 0.3) of the swimmers would be expected to become ill. The same values at geometric means of 200, 500, and 1,000, respectively, would be approximately: 0.9%, 1%, and 1.2%. For persons who did not go into the water, the observed rate of skin illness was 0.25%, using the modelled population. The factors which significantly altered the model are listed in Table 14. They were: interviewer (p=0.0004), contact person (p=0.0140), and age (0.0190).

The graphic depiction of the logistic regression model results for P. aeruginosa (on mPA) versus overall illness is revealed in Figure 9. At a geometric mean bacterial count of 1, approximately 6.5% (+/-2 x 0.1) of the swimmers would be expected to become ill. The same values at geometric means of 10 and 100, respectively, would be approximately 8% and 9.4%. The observed rate of overall illness in persons who did not enter the water was 1.93%, using the same population as the one used in modelling. The factors which significantly altered the model for swimmers becoming ill are outlined in Table 15. They were: age, beach, contact person, and interviewer (p=0.0001), swimming before or after (p=0.0024), and sex (p=0.0216).

Finally, let us consider Tables 16 and 17. These models were generated in order to test the value of existing fecal coliform guidelines in the United States and Ontario. In Table 16, the American guideline was tested, and the bacterial count was divided into two categories (ie: 1) the geometric mean was less than or equal to the guideline of 200 fecal coliforms/100 mL of water, or 2) it was greater than this guideline), as a discrete variable. The important factors which significantly altered the model were: interviewer (p=0.0001), age (p=0.0003), contact person (p=0.0162), and swimming before or after (p=0.0519), and the p value for the chi-square associated with the count was not significant (p=0.2857). Thus, a geometric mean guideline of 200 fecal coliforms/100 mL of water was not a good dividing point for this data, that is, there would be no significant difference in swimmers becoming ill above and below this value. If one examines Table 17, the Ontario guideline of 100 fecal coliforms/100 mL of water was tested, such that the bacterial count was divided into the categories of less than or equal to 100 fecal coliforms/100 mL of water, or greater than 100 fecal coliforms/100 mL of water. The important factors which significantly altered this model were: interviewer (p=0.0001), age (p=0.0002), fecal coliform category (p=0.0127), and contact person (p=0.0153) (sex was included, although it was not significant at a p value of 0.1146, because of borderline significance in the subtraction of loglikelihoods). This suggests that the Ontario guideline was an appropriate dividing point for the data, and there would be significant differences in the right direction, for swimmers becoming ill, above and below this guideline value.

CONCLUSIONS

The findings of this study may be summarized as follows:

1) In general, closure of the beaches investigated during the summer of 1983 had no significant effect on the bacterial counts. A statistically significant increase in total staphylococci was detected at the open versus the closed beaches. This result could reflect staphylococcal shedding by bathers.

2) Logistic regression modelling in swimmers revealed that illness increased as the bacterial counts increased, but not siginificantly at the 5% level. This suggests that further studies should be undertaken in order to evaluate the existing water sampling procedures (two samples, collected daily at a beach might not be representative for the

beach) and postulate other factors which might contribute to the prediction of illness. Perhaps other bacterial indicators or pathogens should be considered. In addition, if the illness detected is primarily virological in nature, then we may need to find an optimum bacterial indicator of virological pollution, and/or improve virological isolation techniques with a view to choosing a virological guideline for recreational water quality.

3) Logistic regression testing of the American and Ontario fecal coliform guidelines for recreational waters revealed that the Ontario guideline is more effective in predicting illness in swimmers. It is recommended that the guideline remain unchanged.

4) Because confounding variables such as: age, contact person, and interviewer have been shown to occur frequently in the logistic regression models in this study, future epidemiological surveys should be designed to minimize these factors.

5) Pending further investigation, it is recommended that the following be employed as recreational freshwater quality indicators: fecal coliforms, total staphylococci (19,20) and P. aeruginosa on mPA. E. coli may also be incorporated.

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Table 1. Summary of Maximum Limits for Coliforms in Primary Contact Recreational Water Presented by Various Agencies

Agency	Sampling Regime	Total Coliforms	Fecal Coliforms	Other	Reference
1. (U.S.) National Technical Advisory Committee	Not less than 5 samples taken over not more than a 30-day period	-	$\leq$200/100 mL, nor shall more than 10% of the samples exceed 400/100 mL	-	National Technical Advisory Committee, 1968
2. Province of British Columbia	Not less than 5 samples taken over not more than a 30-day period	-	Running geometric mean $\leq$200/100 mL, nor shall more than 10% of the samples exceed 400/100 mL	-	Province of British Columbia, 1969
3. Inland Waters Directorate, Department of the Environment	-	$\leq$500/100 mL	$\leq$200/100 mL	-	Environment Canada, 1972
4. Alberta Environment	Not less than 5 samples taken over not more than a 30-day period	Geometric mean $\leq$1000/100 mL	Geometric mean $\leq$200/100 mL	-	Alberta Environment, 1977
5. Ontario Ministries of Health, Environment	At least 10/30 days	Geometric mean $\leq$1000/100 mL	Geometric mean $\leq$100/100 mL	Fecal streptococci, Pseudomonas, Staphylococcus	Ontario Ministry of Health 1975; Ontario Ministry of the Environment, 1978
6. Committee of the Great Lakes Upper Mississippi River Board of State Sanitary Engineers	-	-	Geometric mean $\leq$200/100 mL. No sample to exceed 1000/100 mL	Fecal streptococcus, Pseudomonas	Committee of the Great Lakes Upper Mississippi River Board of State Sanitary Engineers, 1975
7. World Health Organization	-	-	E. coli $\leq$1000/100 mL	-	World Health Organization 1975
8. U.S. Environmental Protection Agency	Not less than 5 samples taken over not more than a 30-day period	-	Geometric mean $\leq$200/100 mL nor shall more than 10% of the samples exceed 400/100 mL	-	U.S. Environmental Protection Agency, 1976
9. Saskatchewan Environment	Not less than 5 samples taken over not more than a 30-day period	Geometric mean $\leq$1000/100 mL	Geometric mean $\leq$200/100 mL	-	Saskatchewan Environment, 1977
10. Manitoba Clean Environment Commission	Not less than 5 samples per month	Median <500 MPN/ 100 mL	Median <200 MPN/100 mL	-	Province of Manitoba, 1979

(from Health and Welfare Canada, 1983;)

Table 2. Record of the Sampling and Closure Dates for the Six Beaches Surveyed in 1983.

	BOYD		CLAIREVILLE		ALBION		HEART LAKE		KELSO		PROFESSOR'S LAKE	
Date Sampled	Open	Closed	Open	Closed	Open	Closed	Open	Closed	Open	Closed	Open	Closed
June 25	x		x		x		x					
June 26	x		x		x		x					
July 1	x		x		x		x					
July 2	x		x		x		x					
July 3	x		x		x		x					
July 9		x	x		x		x					
July 10		x	x		x		x					
July 16		x	x		x		x					
July 17		x	x		x		x					
July 23		x		x	x		x					
July 24		x		x	x		x					
July 30		x		x	x		x		x			
July 31		x		x	x			x	x			
Aug. 1		x		x	x			x	x			
Aug. 6		x		x	x			x		x	x	
Aug. 7		x		x	x			x		x	x	
Aug. 13		x		x	x			x			x	
Aug. 14		x		x	x			x			x	
Aug. 20		x		x	x			x			x	
Aug. 21		x		x	x			x			x	
Aug. 27		x		x	x			x			x	
Aug. 28		x		x	x			x			x	

Table 3. Overall Geometric Means of Bacterial Counts

	Geometric Means					
Organism	Open and Closed Beaches	n	Open Beaches	n	Closed Beaches	n
Pseudomonas aeruginosa (mPA)	7	172	7	118	9	54
Pseudomonas aeruginosa (mTIN)	6	172	6	118	7	54
Heterotrophs	2799063	171	2589361	118	3328985	53
Enterococci	35	172	27	118	61	54
Total staphylococci	125	163	142	109	96	54
Fecal streptococci	100	172	88	118	131	54
Escherichia coli	370	172	361	118	390	54
Fecal coliforms	432	172	423	118	453	54

Table 4. Results from Anova Testing (t tests - LSD) of $\log_e$ Bacteriological Counts by Status (i.e. Open or Closed)*

← Status →	1 = open	2 = closed
1 = open		a e
2 = closed	a e	

__Legend__

a = total staphylococci

b = heterotrophs

c = *E. coli*

d = fecal coliforms

e = enterococci

f = fecal streptococci

g = *P. aeruginosa* (mPA)

h = *P. aeruginosa* (mTIN)

*Only comparisons which are statistically significantly different (at the 0.05 level) are listed.

Table 5. Geometric Means of Bacterial Counts by Month

Organism	Geometric Means for:					
	June	n	July	n	August	n
P. aeruginosa (mPA)	5	16	10	91	6	65
P. aeruginosa (mTIN)	6	16	8	91	4	65
Heterotrophs	6990824	16	3956978	91	1360989	64
Enterococci	4	16	45	91	41	65
Total staphylococci	291	8	169	90	74	65
Fecal streptococci	123	16	142	91	58	65
E. coli	272	16	479	91	278	65
Fecal coliforms	310	16	555	91	330	65

Table 6. Results from Anova Testing (t tests - LSD) of Log_e Bacteriological Counts by Month*

Month	6	7	8
6		b e	a b e f
7	b e		a b c d f
8	a b e f	a b c d f	

Legend

a = total staphylococci

b = heterotrophs

c = *E. coli*

d = fecal coliforms

e = enterococci

f = fecal streptococci

g = *P. aeruginosa* (mPA)

h = *P. aeruginosa* (mTIN)

*Only comparisons which are statistically significantly different (at the 0.05 level) are listed.

Table 7. Geometric Means of Bacterial Counts by Beach

i) For open and Closed Beaches

Beach	n**	*P. aeruginosa* (mPA)	*P. aeruginosa* (mTIN)	Heterotrophs	Enterococci	Total staphylococci	Fecal streptococci	*E. coli*	Fecal coliforms
• Boyd C.A.*	39	18	11	6033695	37	103	152	443	503
• Claireville C.A.	31	8	6	2407375	72	282	203	794	967
• Albion Hills C.A.	44	4	4	3174590	19	93	55	298	327
• Heart Lake	34	6	5	3216177	39	176	120	224	268
• Kelso C.A.	8	30	17	1540471	77	180	125	1147	1283
• Professor's Lake	16	4	3	412746	22	41	29	163	216

CA • Conservation Area.

* For total staphylococci n = 37, 28, 42, 32, 8, 16

ii) For open Beaches

beach	n**	*P. aeruginosa* (mPA)	*P. aeruginosa* (mTIN)	Heterotrophs	Enterococci	Total staphylococci	Fecal streptococci	*E. coli*	Fecal coliforms
	10	12	8	16323929	29	391	272	1102	1275
	18	13	9	4563167	46	502	200	624	763
	44	4	4	3174590	19	93	55	298	327
	24	7	7	2279226	27	217	116	251	300
	6	61	27	1100521	116	160	244	1619	1799
	16	4	3	412746	22	41	29	163	216

** For total staphylococci n = 8, 15, 42, 22, 6, 16

iii) For Closed Beaches

Beach	n****	*P. aeruginosa* (mPA)	*P. aeruginosa* (mTIN)	Heterotrophs	Enterococci	Total staphylococci	Fecal streptococci	*E. coli*	Fecal coliforms
1	29	21	13	4280896	40	72	125	324	365
2	13	4	4	993127	131	145	206	1107	1343
3	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	10	3	3	8056505	94	110	127	170	204
5	2	4	4	4224926	22	255	17	408	465
6	NA	NA	NA	NA	NA	NA	NA	NA	NA

****: For heterotrophs n = 29, 13, NA, 9, 2, NA.

Table 8. Results from Anova Testing (t tests - LSD) of $\log_e$ Bacteriological Counts by Beach*

← Beach →

Beach	1	2	3	4	5	6
1		a b e	b f g h	a c d g	b	a b c d f g h
2	a b e		a c d e f	c d	g	a b c d e f
3	b f g h	a c d e f		e f	c d e g h	a b
4	a c d g	c d	e f		c d g h	a b f
5	b	g	c d e g h	c d g h		a b c d f g h
6	a b c d f g h	a b c d e f	a b	a b f	a b c d f g h	

Legend

a = total staphylococci

b = heterotrophs

c = *E. coli*

d = fecal coliforms

e = enterococci

f = fecal streptococci

g = *P. aeruginosa* (mPA)

h = *P. aeruginosa* (mTIN)

*Only comparisons which are statistically significantly different (at the 0.05 level) are listed.

Table 9. Results from Anova Testing (t tests - LSD) of $\log_e$ Bacteriological Counts by Beach and Status*

← Beach and Status Code →

Beach and Status Code	11	12	13	14	15	16	21	22	23 (not applicable)	24	25	26 (not applicable)
11		b	a b c d f g	b c d f	b g	a b c d f	a b c d f	b e		a c d	f	
12	b		a c d e f g	b c d	b g	a b c d f g h	a d f	a b e g		a c d g	f	
13	a b c d f g	a c d e f g		a f	b c d e f g h	a b f	a g h	b c d e f		b e f		
14	b c d f	b c d	a f		c d e g h	a b f	a g	b c d e		b e	f	
15	b g	b g	b c d e f g h	c d e g h		a b c d e f g h	a b c d f	g h		b c d g h	f g	
16	a b c d f	a b c d f g h	a b f	a b f	a b c d e f g h		b f g h	a b c d e f		b e f	b	
21	a b c d f	a d f	a g h	a g	a b c d f	b f g h		a b c d e f g		a b g h	f	
22	b e	a b e g	b c d e f	b c d e	g h	a b c d e f	a b c d e f g			b c d	f	
23 (not applicable)												
24	a c d	a c d g	b e f	b e	b c d g h	b e f	a b g h	b c d			f	
25	f	f		f	f g	b	f	f		f		
26 (not ap-												

Legend - letters
a = total staphylococci
b = heterotrophs
c = *E. coli*
d = fecal coliforms
e = enterococci
f = fecal streptococci
g = *P. aeruginosa* (mPA)
h = *P. aeruginosa* (mTIN)

Legend - numbers
11 = Beach 1 (Boyd) - open
12 = Beach 2 (Claireville) - open
13 = Beach 3 (Albion) - open
14 = Beach 4 (Heart Lake) open
15 = Beach 5 (Kelso) - open
16 = Beach 6 (Professor's) - open
21 = Beach 1 - closed
22 = Beach 2 - closed
23 = Beach 3 - closed
24 = Beach 4 - closed
25 = Beach 5 - closed
26 = Beach 6 - closed

Note:
Beach 3 and Beach 6 were never closed. Thus, 23 and 26 columns are blank.

Table 10. Response Rates Achieved in the Epidemiological Study

Interviewed subjects	
No. persons interviewed	10287
No. completed interviews	9296
No. incompleted interviews *	991
% success	90.37

*No answer, wrong number, not-in-service.

Table 11. Crude Symptom Rates for Study Population used in Regression Modelling

i) By water (wade or swim), no water

Symptom	Water (n = 7227) (%) (85.83%)	No water (n = 1193) (%) (14.17%)	p Value*
Ill	7.40	1.93	< .0001
Respiratory	3.11	0.59	< .0001
Gastrointestinal	2.12	0.50	< .0001
Skin	0.79	0.25	.0398
Eye	0.89	0.25	.0206
Ear	0.93	0.17	.0046
Allergy	0.47	0.17	.2254
Other	1.48	0.34	.0005
(Sunburn - not considered an illness	9.78	5.70	< .0001

ii) By wade, swim, no water

Symptom	Wader (n = 574) (%) (6.82%)	Swimmer (n = 6653) (%) (79.01%)	No water (n = 1193) (%) (14.17%)	p Value**
Ill	4.18	7.68	1.93	.0001
Respiratory	1.57	3.25	0.59	.0001
Gastro-intestinal	1.57	2.16	0.50	.0004
Skin	0.17	0.84	0.25	.0235
Eye	0.52	0.92	0.25	.0438
Ear	0.52	0.96	0.17	.0141
Allergy	0.52	0.47	0.17	.3254
Other	1.39	1.49	0.34	.0056
(Sunburn - not considered an illness	7.49	9.98	5.70	.0001

* = By Fisher's exact two-tailed test

** = By chi-square

Table 12. FUNCAT Logistic Regression Model for the Prediction of Gastrointestinal Illness in Swimmers (using Fecal Coliforms)

$$
\begin{aligned}
\text{logit } p = \log_e \left(\frac{p}{1-p}\right) = & - 5.314 \text{ (intercept, or mean illness rate)} \\
& + (0.347 \times \log_{10} \text{ fecal coliform count}^{*}) \\
& \begin{cases} +0.268 & \text{(if contact person)} \\ -0.268 & \text{(if contact person)} \end{cases} \\
& -(0.032 \times \text{age}) \\
& \begin{cases}
+1.039 & \text{(if interviewer = 1)} \\
+3.078 & \text{(if interviewer = 2)} \\
+1.799 & \text{(if interviewer = 3)} \\
+0.495 & \text{(if interviewer = 4)} \\
+0.138 & \text{(if interviewer = 5)} \\
+1.508 & \text{(if interviewer = 6)} \\
+0.420 & \text{(if interviewer = 7)} \\
+1.803 & \text{(if interviewer = 8)} \\
+1.823 & \text{(if interviewer = 9)} \\
-7.857 & \text{(if interviewer = 10)} \\
-7.930 & \text{(if interviewer = 11)} \\
+0.747 & \text{(if interviewer = 12)} \\
+1.742 & \text{(if interviewer = 13)} \\
+1.195 & \text{(if interviewer = 14)}
\end{cases}
\end{aligned}
$$

Notes:

1. p = ill with gastrointestinal symptoms

   1-p = not ill with gastrointestinal symptoms.

* Each count is a geometric mean by beach, month, and date.

Table 12. continued

2. In the model the effects of the factors involved are as follows:

Source	Df (degrees of freedom)	χ^{2**} value	χ^2 p value
Intercept	1	0.74	0.3905
Log_{10} fecal coliform count	1	2.91	0.0881
Contact person	1	6.02	0.0141
Age	1	15.57	0.0001
Interviewer	13	52.85	0.0001
Likelihood ratio	154	988.32	1.0000

** Chi-square.

Table 13. FUNCAT Logistic Regression Model for the Prediction of Gastrointestinal Illness in Swimmers (using *E. coli*)

$$\text{logit } p = \log_e\left(\frac{p}{1-p}\right) = -5.240 \quad \text{(intercept, or mean illness rate)}$$

$$+(0.325 \times \log_{10} \text{ \underline{E. coli} count*})$$

$$\begin{cases} +0.268 & \text{(if contact person)} \\ -0.268 & \text{(if not contact person)} \end{cases}$$

$$-(0.032 \times \text{age})$$

$$\begin{cases} +1.012 & \text{(if interviewer = 1)} \\ +3.088 & \text{(if interviewer = 2)} \\ +1.798 & \text{(if interviewer = 3)} \\ +0.501 & \text{(if interviewer = 4)} \\ +0.126 & \text{(if interviewer = 5)} \\ +1.506 & \text{(if interviewer = 6)} \\ +0.428 & \text{(if interviewer = 7)} \\ +1.811 & \text{(if interviewer = 8)} \\ +1.836 & \text{(if interviewer = 9)} \\ -7.865 & \text{(if interviewer =10)} \\ -7.956 & \text{(if interviewer =11)} \\ +0.771 & \text{(if interviewer =12)} \\ +1.747 & \text{(if interviewer =13)} \\ +1.197 & \text{(if interviewer =14)} \end{cases}$$

Notes:

1. p = ill with gastrointestinal symptoms.

   1-p = not ill with gastrointestinal symptoms.

* Each count is a geometric mean by beach, month, and date.

2. In the model the effects of the factors involved are as follows:

Source	Df (Degrees of Freedom)	χ^{2**} Value	χ^2 p value
Intercept	1	0.72	0.3971
Log_{10} *E. coli* count	1	2.67	0.1021
Contact person	1	6.03	0.0141
Age	1	15.54	0.0001
Interviewer	13	52.87	0.0001
Likelihood ratio	154	988.54	1.0000

** Chi-square.

Table 14. FUNCAT Logistic Regression Model for the Prediction of Skin Illness in Swimmers (using Total Staphylococci)

$$\text{logit } p = \log_e\left(\frac{p}{1-p}\right) = -7.390 \text{ (intercept, or mean illness rate)}$$

$$+\ (0.560 \times \log_{10} \text{ total staphylococci count}^*)$$

$$\begin{cases} +0.408 & \text{(if contact person)} \\ -0.408 & \text{(if not contact person)} \end{cases}$$

$$-\ (0.0310 \times \text{age})$$

$$\begin{cases} +2.790 & \text{(if interviewer = 1)} \\ -6.853 & \text{(if interviewer = 2)} \\ +2.460 & \text{(if interviewer = 3)} \\ +1.057 & \text{(if interviewer = 4)} \\ +1.909 & \text{(if interviewer = 5)} \\ +3.374 & \text{(if interviewer = 6)} \\ +0.237 & \text{(if interviewer = 7)} \\ +3.004 & \text{(if interviewer = 8)} \\ +2.317 & \text{(if interviewer = 9)} \\ -7.104 & \text{(if interviewer =10)} \\ -7.179 & \text{(if interviewer =11)} \\ +2.079 & \text{(if interviewer =12)} \\ +1.160 & \text{(if interviewer =13)} \\ +0.749 & \text{(if interviewer =14)} \end{cases}$$

Notes:

1. p = ill with skin symptoms
2. 1-p = not ill with skin symptoms.

* Each count is a geometric mean by beach, month and date.

2. In the model the effects of the factors involved are as follows:

Source	Df(Degrees of Freedom)	χ^{2**} value	χ^2 p value
Intercept	1	0.38	0.5352
Log_{10} total staphylococci count	1	2.79	0.0947
Contact person	1	6.04	0.0140
Age	1	5.50	0.0190
Interviewer	13	36.81	0.0004
Likelihood ratio	154	498.76	1.0000

** Chi-square

Table 15. "UNCA" Logistic Regression Model for the Prediction of Illness in Swimmers (using *P. aeruginosa* (on mPA))

$$\text{logit } p = \log_e\left(\frac{p}{1-p}\right) = -2.209 \text{ (intercept, or mean illness rate)}$$

$$+(0.182 \times \log_{10} \textit{P. aeruginosa} \text{ count}^*)$$

$$\begin{cases} +0.393 \text{ (if contact person)} \\ -0.393 \text{ (if not contact person)} \end{cases}$$

$$\begin{cases} +0.146 \text{ (if swam before or after)} \\ -0.146 \text{ (if swam before or after)} \end{cases}$$

$$-(0.027 \times \text{age})$$

$$\begin{cases} -0.176 & \text{(if beach 1)} \\ +0.196 & \text{(if beach 2)} \\ +0.253 & \text{(if beach 3)} \\ +0.507 & \text{(if beach 4)} \\ -0.430 & \text{(if beach 5)} \\ -0.358 & \text{(if beach 6)} \end{cases}$$

$$\begin{cases} -0.341 & \text{(if interviewer = 1)} \\ +0.767 & \text{(if interviewer = 2)} \\ +0.759 & \text{(if interviewer = 3)} \\ +0.127 & \text{(if interviewer = 4)} \\ -0.629 & \text{(if interviewer = 5)} \\ +0.486 & \text{(if interviewer = 6)} \\ -0.191 & \text{(if interviewer = 7)} \\ +0.620 & \text{(if interviewer = 8)} \\ +0.477 & \text{(if interviewer = 9)} \\ -1.302 & \text{(if interviewer =10)} \\ -0.665 & \text{(if interviewer =11)} \\ -0.370 & \text{(if interviewer =12)} \\ +0.618 & \text{(if interviewer =13)} \\ -0.356 & \text{(if interviewer =14)} \end{cases}$$

*Each count is a geometric mean by beach, month, and data.

$$\begin{cases} -0.109 \text{ (if sex = male)} \\ +0.109 \text{ (if sex = female)} \end{cases}$$

Notes:

1. p = ill.
   1-p = not ill.

2. In the model the effects of the factors involved are as follows:

Source	Df (Degrees of freedom)	X^{2**} value	X^2 p value
Intercept	1	136.41	0.0001
$\log_{10}$ *P. aeruginosa* count	1	2.37	0.1237
Contact person	1	46.09	0.0001
Swimming before or after	1	9.22	0.0024
Age	1	35.64	0.0001
Beach	5	25.03	0.0001
Interviewer	13	65.97	0.0001
Sex	1	5.27	0.0216
Likelihood ratio	463	3023.41	1.0000

** Chi-square.

Table 16. FUNCAT Logistic Regression Model for the Prediction of Gastrointestinal Illness in Swimmers (using two categories for fecal coliform count*) - U.S. Guideline** Testing

$$\text{logit } p = \log_e\left(\frac{p}{1-p}\right) = -4.489 \text{ (intercept, or mean illness rate)}$$

$$\left\{\begin{array}{l} -0.123 \text{ (if geometric mean of fecal coliform count 0-200)} \\ +0.123 \text{ (if geometric mean of fecal coliform count >200)} \end{array}\right.$$

$$\left\{\begin{array}{l} +0.263 \text{ (if contact person)} \\ -0.263 \text{ (if not contact person)} \end{array}\right.$$

$$\left\{\begin{array}{l} +0.169 \text{ (if swam before or after)} \\ -0.169 \text{ (if swam before or after)} \end{array}\right.$$

$$-(0.030 \times \text{age})$$

$$\left\{\begin{array}{ll} +1.091 & \text{(if interviewer = 1)} \\ +3.032 & \text{(if interviewer = 2)} \\ +1.815 & \text{(if interviewer = 3)} \\ +0.507 & \text{(if interviewer = 4)} \\ +0.091 & \text{(if interviewer = 5)} \\ +1.497 & \text{(if interviewer = 6)} \\ +0.447 & \text{(if interviewer = 7)} \\ +1.797 & \text{(if interviewer = 8)} \\ +1.829 & \text{(if interviewer = 9)} \\ -7.963 & \text{(if interviewer =10)} \\ -7.979 & \text{(if interviewer =11)} \\ +0.846 & \text{(if interviewer =12)} \\ +1.787 & \text{(if interviewer =13)} \\ +1.203 & \text{(if interviewer =14)} \end{array}\right.$$

* 1) geometric mean 0-200 = category 1.
2) geometric mean > 200 = category 2.

Note: 200 is the U.S. guideline.

** (National Technical Advisory Committee, 1968)

Notes

1. p = ill with gastrointestinal symptoms.
   1-p = not ill with gastrointestinal symptoms.

2. In the model the effects of the factors involved are as follows:

Source	Df(degrees of freedom)	χ^{2**} value	χ^2 p value
Intercept	1	0.53	0.4657
Fecal coliform category	1	1.14	0.2857
Contact person	1	5.79	0.0162
Swimming before of after	1	3.78	0.0519
Age	1	13.24	0.0003
Interviewer	13	50.61	0.0001
Likelihood ratio	226	715.38	1.000

** Chi-square.

Table 17. FUNCAT Logistic Regression Model for the Prediction of Gastrointestinal Illness in Swimmers (using two categories for fecal coliform count*) - Ontario Guideline** Testing

$$\text{logit } p = \log_e\left(\frac{p}{1-p}\right) = -5.144 \text{ (intercept), or mean; illness rate)}$$

$$\begin{cases} -0.736 & \text{(if geometric mean of fecal coliform count 0-100)} \\ +0.736 & \text{(if geometric mean of fecal coliform count >100)} \end{cases}$$

$$\begin{cases} +0.266 & \text{(if contact person)} \\ -0.266 & \text{(if not contact person)} \end{cases}$$

$$\begin{cases} +0.166 & \text{(if swam before or after)} \\ -0.166 & \text{(if swam before or after)} \end{cases}$$

$$-(0.031 \times \text{age})$$

$$\begin{cases} +0.894 & \text{(if interviewer = 1)} \\ +3.056 & \text{(if interviewer = 2)} \\ +1.856 & \text{(if interviewer = 3)} \\ +0.552 & \text{(if interviewer = 4)} \\ +0.124 & \text{(if interviewer = 5)} \\ +1.517 & \text{(if interviewer = 6)} \\ +0.481 & \text{(if interviewer = 7)} \\ +1.911 & \text{(if interviewer = 8)} \\ +1.913 & \text{(if interviewer = 9)} \\ -8.021 & \text{(if interviewer = 10)} \\ -8.199 & \text{(if interviewer = 11)} \\ +0.867 & \text{(if interviewer = 12)} \\ +1.823 & \text{(if interviewer = 13)} \\ +1.226 & \text{(if interviewer = 14)} \end{cases}$$

$$\begin{cases} -0.136 & \text{(if sex = male)} \\ +0.136 & \text{(if sex = female)} \end{cases}$$

* 1) geometric mean 0 - 100 = category 1.
  2) geometric mean $\geq$100 = category 2.
** Health and Welfare Canada, 1981)

Notes

1. p = ill with gastrointestinal symptoms.
   1-p = not ill with gastrointestinal symptoms.

2. In the model the effects of the factors involved are as follows:

Source	Df (Degrees of Freedom)	χ^{2**} Value	χ^2 p value
Intercept	1	0.70	0.4035
Fecal coliform category	1	6.21	0.0127
Contact person	1	5.89	0.0153
Swimming before or after	1	3.67	0.0553
Age	1	13.50	0.0002
Interviewer	13	52.56	0.0001
Sex	1	2.49	0.1146
Likelihood ratio	798	814.64	1.0000

** Chi-square.

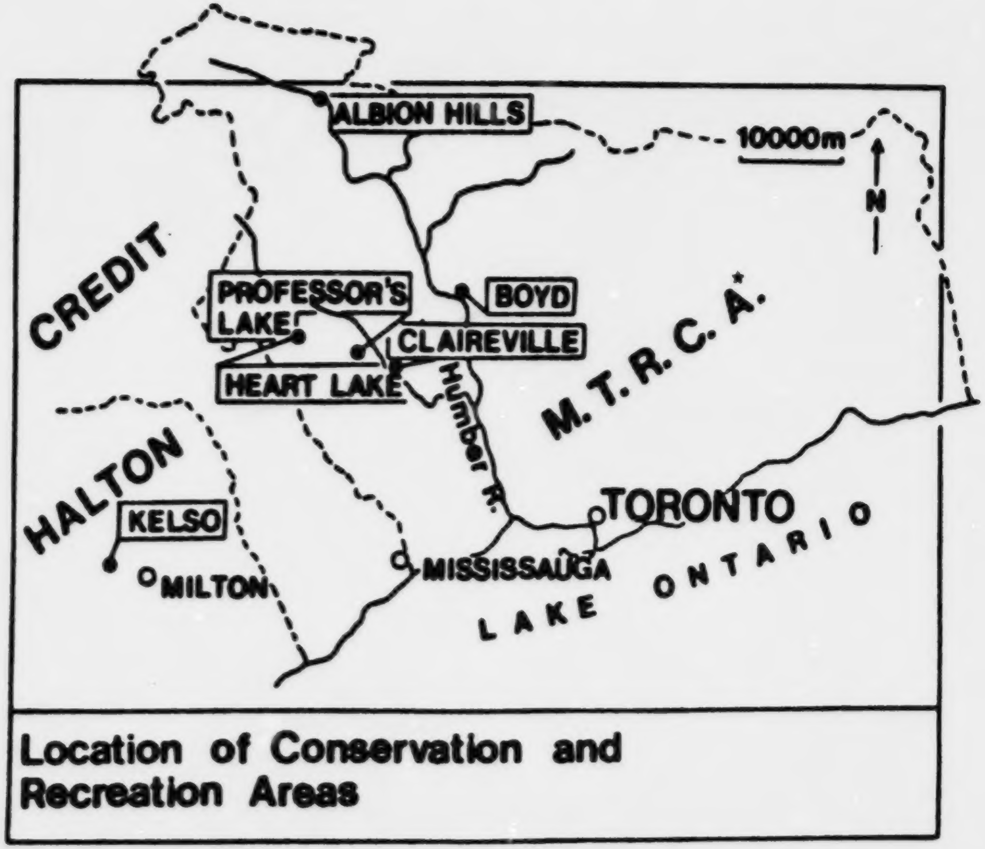

ALBION HILLS
10000m
N
CREDIT
PROFESSOR'S LAKE
BOYD
M.T.R.C.A.*
CLAIREVILLE
HEART LAKE
Humber R.
HALTON
KELSO
MILTON
MISSISSAUGA
TORONTO
LAKE ONTARIO
Location of Conservation and Recreation Areas

Figure 1. Location of Sample Sites

* Metropolitan Toronto Regional Conservation Authority.

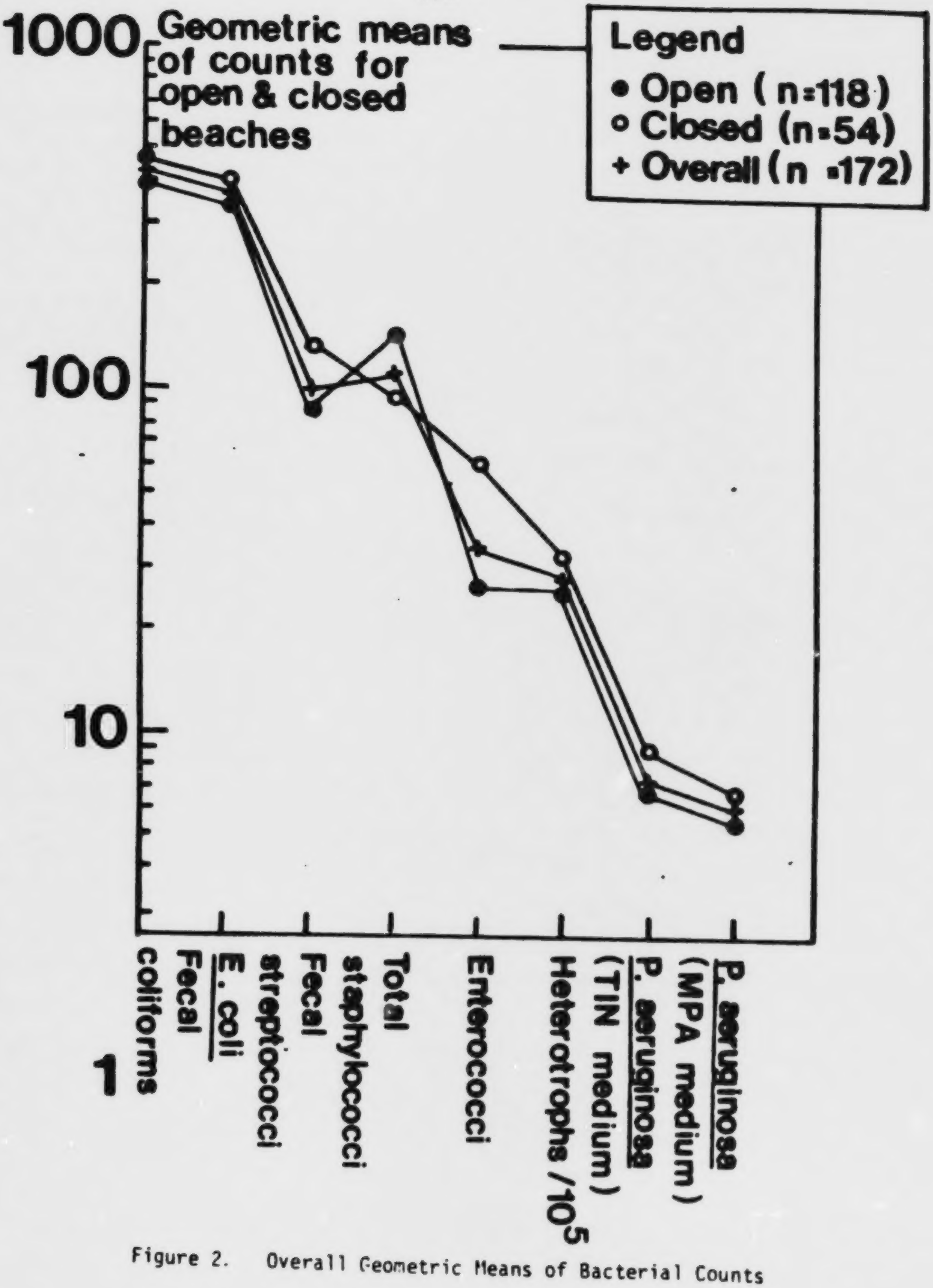


Figure 2. Overall Geometric Means of Bacterial Counts

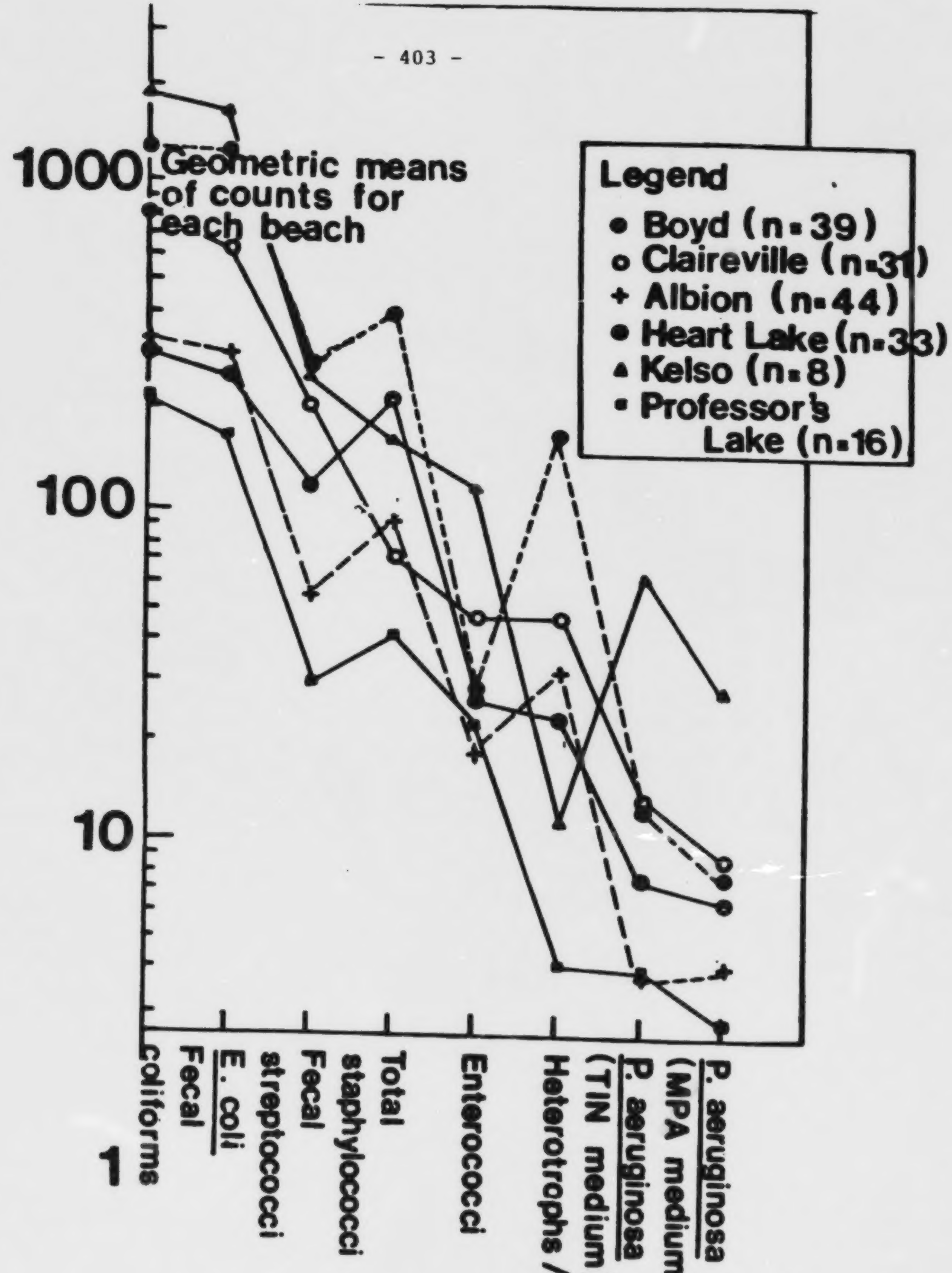


Figure 3. Geometric Means of Bacterial Counts by Beach

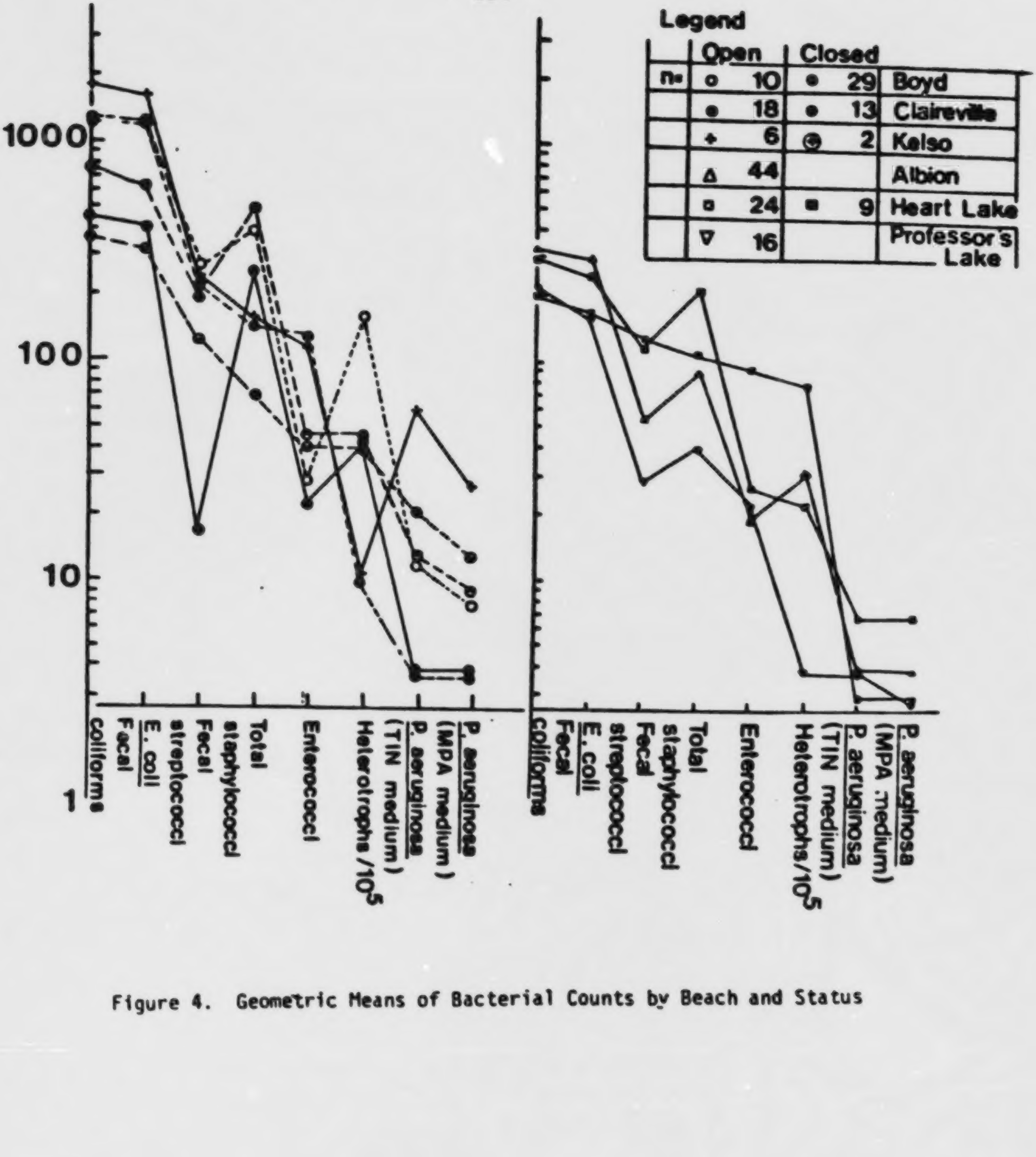


Figure 4. Geometric Means of Bacterial Counts by Beach and Status

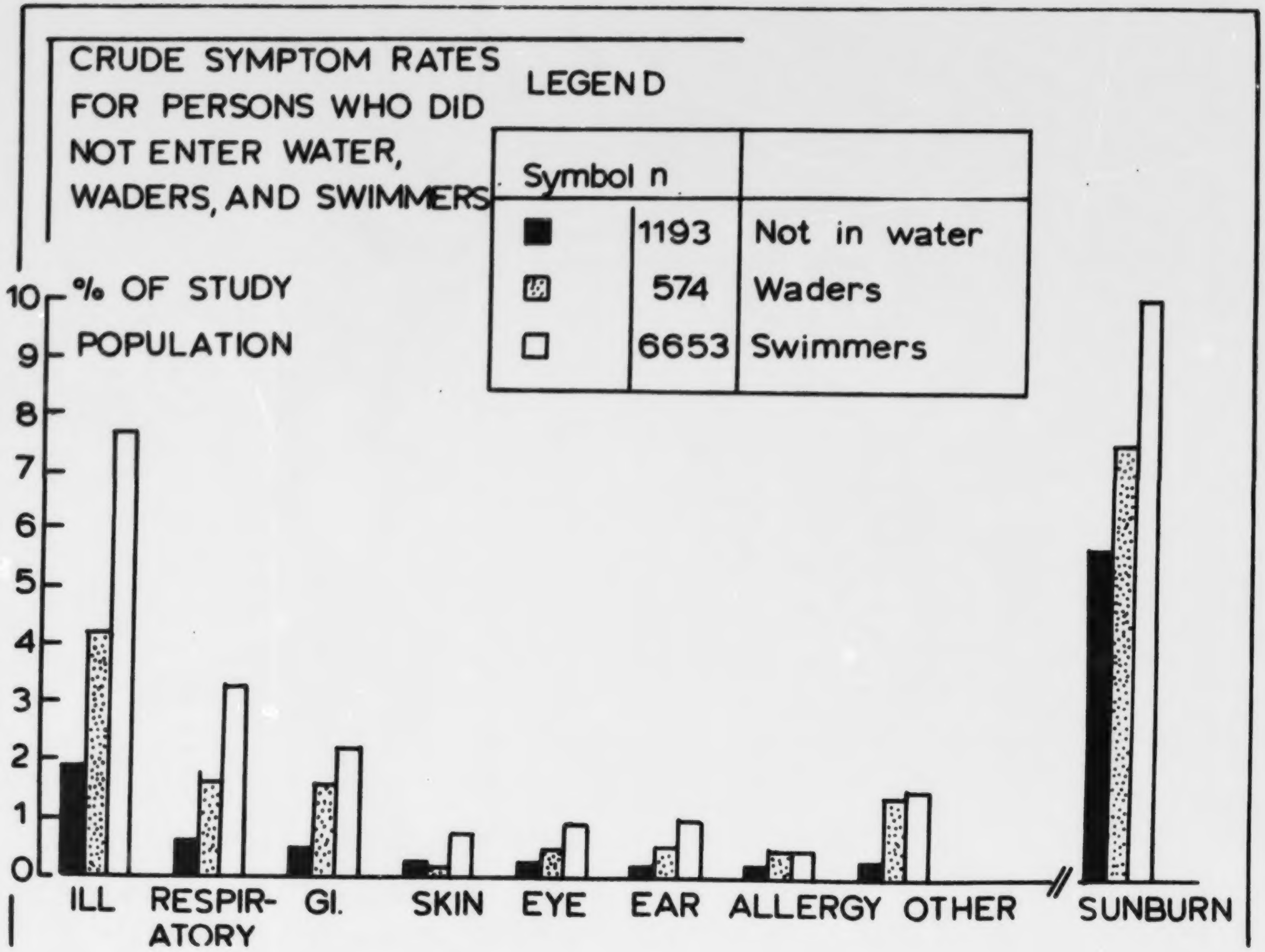


Figure 5. Crude Symptom Rates for the Study Population used in Regression Modelling

Figure 6. Graphic Representation of Logistic Regression Model Results for Fecal Coliforms Versus Gastrointestinal Illness.

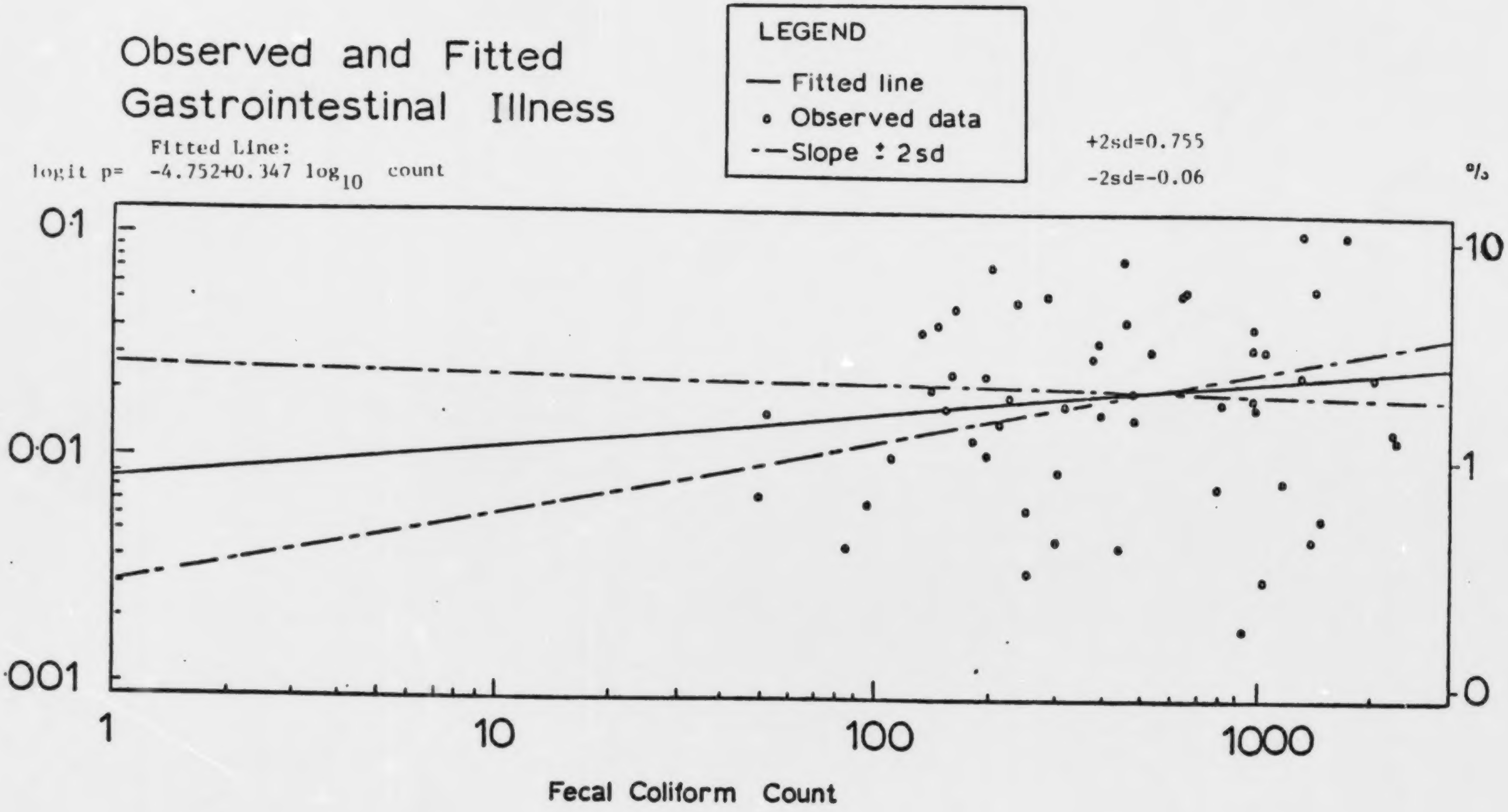


Figure 7. Graphic Representation of Logistic Regression Model Results for *E. coli* versus Gastrointestinal Illness

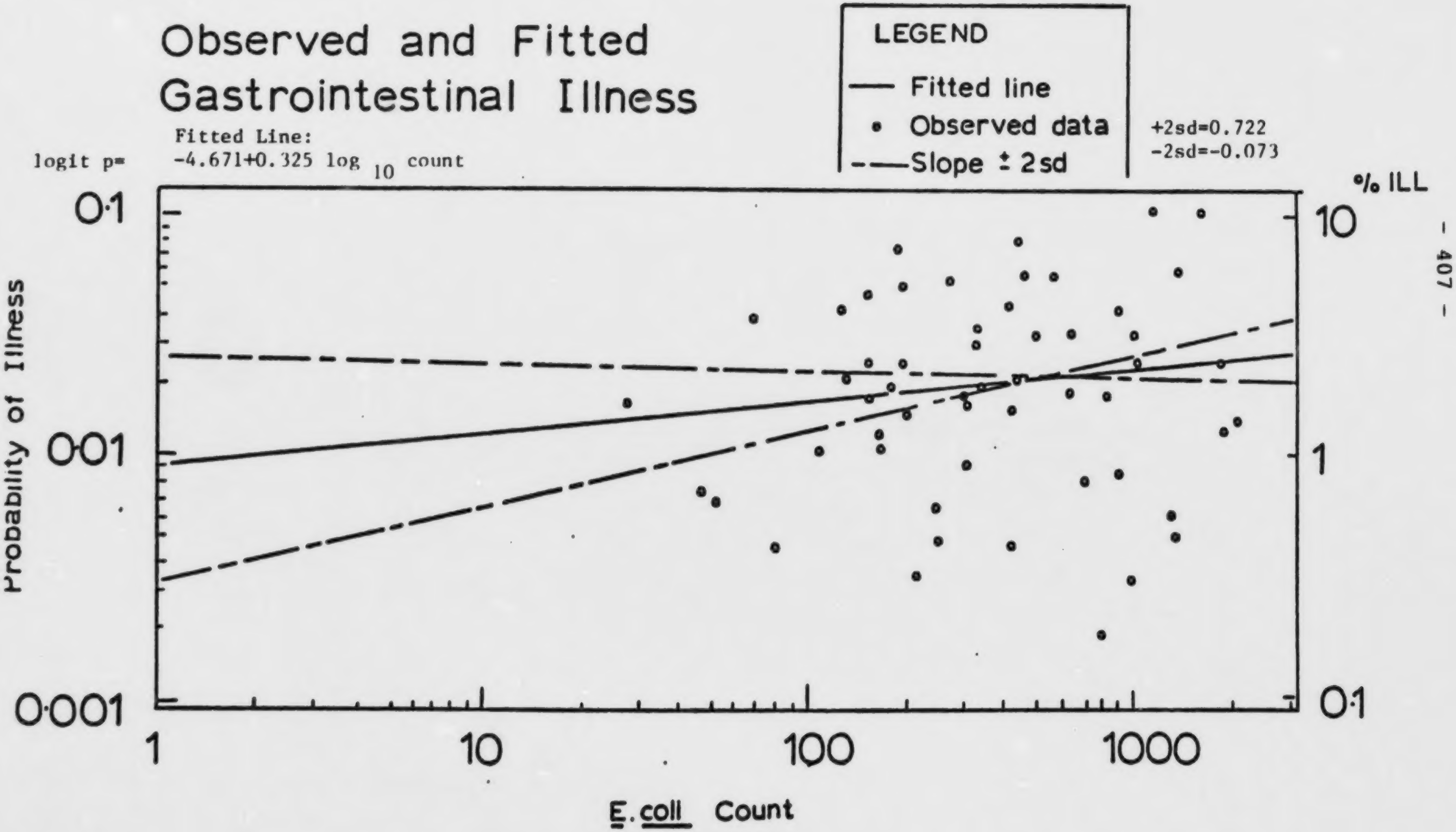


Figure 8. Graphic Representation of Logistic Regression Model Results for Total Staphylococci versus Skin Illness.

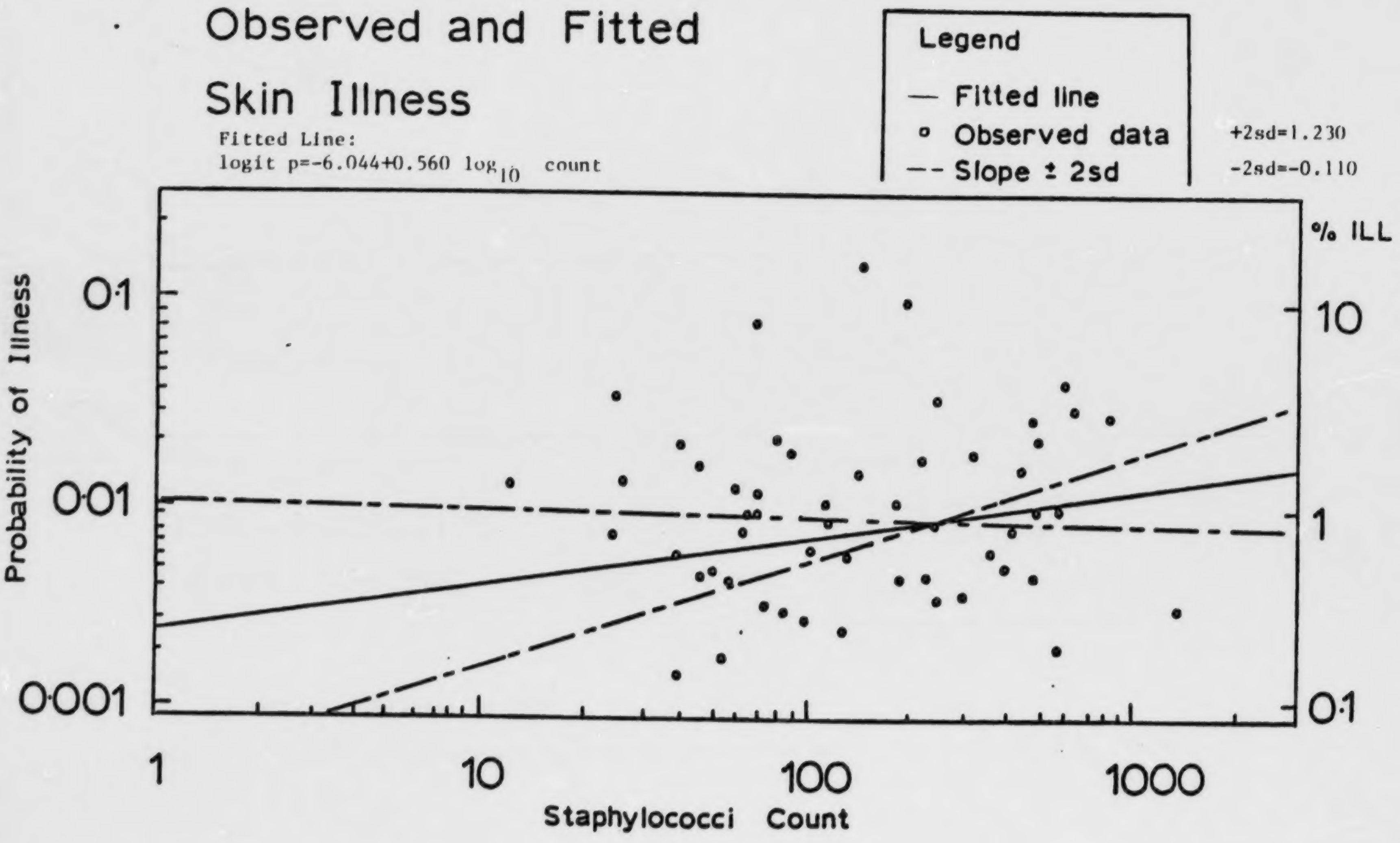
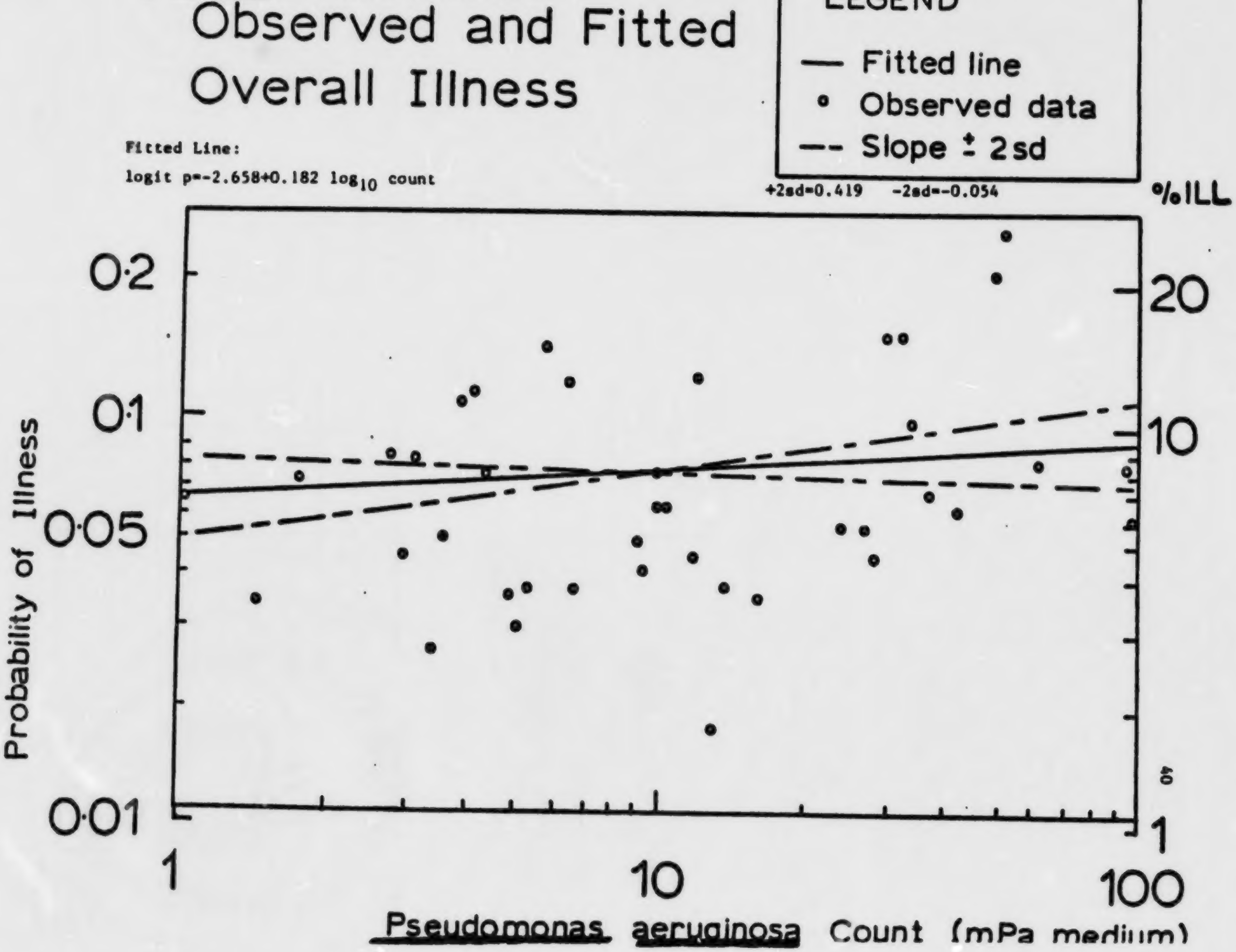


Figure 9. Graphic Representation of Logistic Regression Model Results for *P. aeruginosa* (mPA) versus Overall Illness.



Appendix -1-

INITIAL INTERVIEW FORM

1

DATE: ☐☐☐☐ TIME: ☐☐☐☐ I.D. ☐☐☐☐☐☐☐☐☐

LEGEND: YES - 1 NO - 2 NOT APPLICABLE = blank

I. GIVEN, SURNAMES (1st then 2nd)	1.	2.	3.	4.	5.	6.
II. RELATIONSHIP TO CONTACT PERSON						
III. AGE (exact)						
& SEX (M=1, F=2)						
IV. SWAM IN PAST 4 DAYS? (Yes or No) OR, WADED						
OTHER PLACE?						
HEAD UNDER?						
V. SWAM, OR WILL SWIM TODAY?						
HEAD UNDER?						
VI. ITALIAN						
VII CONTACT PERSON ONLY:						
Mother						
No. persons in household?						
No. rooms in household?						

PHYSICAL SYMPTOMS ("1" for current;
("2" for past 4 days)
BLANK IF NONE

1. COLD, UPPER RESPIRATORY						
2. EAR PROBLEMS						
3. STYES OR BOILS						
4. GASTROINTESTINAL						
5. ALLERGIES						
6. SUNBURN						
7. OTHER (NOTE)						

CONTACT PERSON'S FULL NAME			
ADDRESS			NOTES
POSTAL CODE			
PHONE NO.			
BEST TIME TO CALL			

12

TELEPHONE FOLLOWUP FORM

DATE: ☐☐☐☐ I.D. ☐☐☐☐☐☐☐☐☐

LEGEND: 1 - YES 2 = NO NOT APPLICABLE = blank

NAME						
I. Swam on contact day?						
In water 10 or more min. on contact day						
Head under?						
Just waded (feet in) on contact day						
Swam 10 or more min.?						
II. Swam in next 3 days?						
Which days? 1=Sun. 2=M 3=T 4=W 5=Sat.						
At this beach only? (Yes or No)						
Head under? (Yes or No) 1 2						

III. Swallow any water whilst swimming						
Did not eat food or drink at beach						
Eat food bought at beach (or drink)?						
Eat food, at beach, brought from home (or drink)						

PHYSICAL SYMPTOMS - record only for 3 days after!
(Write in when first noticed) i.e. 1 = 1 day after, 2 = 2, 3 = 3
Blank if none. 4 = contact day.

A. Sore throat						
B. Fever						
C. Cold or cough						
D. Runny or stuffed nose						
E. Earache, Runny Ears						
F. Styes or red, itchy or watery eyes						
G. Stomach ache or nausea						
H. Diarrhea*						
I. Vomiting						
J. Boils						
K. Skin rash						
L. Allergenic itch, welts or sneezing						
M. Sunburn:						
N. Other symptoms						
O. Persons in res. with similar symptoms (not at beach)						
P. Did you see doctor?						
Q. Diagnosis? Give in 2nd box.						
R. Did you stay at home because of illness?						
S. How many days?						

T. If illness serious, may we have your doctor's name and phone number?

Appendix -3-

P. aeruginosa Isolation Medium mPA (Ministry of the Environment Modification)

L - lysine monohydrochloride	5.0 g
Sodium chloride	-
Yeast extract	2.0 g
Xylose	2.5 g
Sodium thiosulfate	5.0 g
Sucrose	1.25 g
Lactose	1.25 g
Magnesium sulphate	1.5 g
Ferric ammonium citrate	0.8 g
Sodium desoxycholate	0.1 g
Phenol red	0.08 g
Agar*	15.0 g
Distilled water (sterile)	800 mL

*Add ingredients, except agar, to sterile beaker. Adjust pH to 7.60 and then add agar. Heat to 93°C until agar starts to dissolve. Do not autoclave. Cool to 70°C, check surface pH (5 mL of mPA in a small plate). Adjust pH if necessary. Cool to 50-55°C (no higher than 60°C). Add antibiotics, mix thoroughly, and pour into petri dishes. Final surface pH 7.1 ± 0.1.

Antibiotics

Sulfapyridine	0.088 g
Kanamycin sulfate	0.0085 g
Nalidixic acid	0.037 g
Actidione	0.15 g

Dissolve in 200 mL sterile H_2O. Heat gently to above 50°C.

BNP Broth

Brucella broth (Gibco) was supplemented with 0.2% Fe So_4.7H20 and autoclaved at 121°C. The broth was cooled to 55°C and supplemented with vancomycin 15.0 mg/L; Trimethoprin 7.5 mg/L; Polymyxin B 30,000 iu/L; sodium bisulfate 0.025%; and sodium pyruvate 0.05%.

Appendix -4-

ENUMERATION AND ISOLATION OF LEGIONELLA PNEUMOPHILA FROM WATER BY DIRECT PLATING PROCEDURE

(Canada Centre for Inland Waters)

Sample Collection

Filter 1000 ml water sample or 100 ml sewage sample through one or more membrane filters. With a sterile 10 ml pipette 10 ml of sterile filtrate is removed and placed into an ointment jar.

The membrane filter is placed into the ointment jar, bacteria containing side down.

Sample Processing

Place capped ointment jar in sonic sink for 10 min. to dislodge bacteria from membrane filter.

1 ml of filtrate-bacteria mixture is removed and placed in capped test tube.
Add 1 ml pH 2.0 buffer, mix and let stand for 10 min.
Add 1 ml neutralizer, mix and using 1 ml pipette, dispense 0.1 ml, 0.3 ml and 0.6 ml of neutralized mixture onto the surface of 3 predried labelled BCYE agar plates.

Using glass spreader, spread inoculum over the surface of the BCYE agar. After the surface of the agar has dried, invert the petri dishes, place in plastic bags, seal and place in 37°C incubator for 4 to 5 days.

Screening Plates

Count all grey-white flat colonies (3-4 mm) with opaque centres, often having ground glass appearance.

Select all or typical representative colonies and with wire loop transfer each colony to

a) BCYE agar 37°C, b) BCYE agar 20°C

c) Tryptone Soya Agar 37°C d) Tryptone Soya Agar 20°C

Incubate the 37° plates for 3 days and the 20°C plates for 7 days. (Each plate may be divided into 4-6 sections to accommodate more colonies.

Only those colonies growing on BCYE agar incubated at 37°C should be considered as potential *Legionella pneumophila*.

Calculations

The total number of Legionella pneumophia per original sample may be derived from the following formula:

$T = N \times (\underline{A}) \times 10.$ Where T = total number bacteria per org. sample volume
N = number of typical colonies per plate
A = total volume of pH treated sample
B = total volume of pH treated sample plated

FINGERPRINTING THE TORONTO WATERFRONT: A METHOD FOR DETERMINING THE SOURCES OF BACTERIAL POLLUTANTS

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and University of Toronto

Key words: Ontario Beaches, Lake Ontario, Fecal Contamination.

ABSTRACT

Utilizing restriction endonucleases, a method of "gene fingerprinting" has been devised. As a molecular epidemiologic tool, the method has important applications in establishing specific epidemiological criteria such as defining the sources and routes of transmission of infectious agents.

We have applied the method to outstanding questions related to bacterial pollution at the Toronto waterfront. Using total DNA extracted from Streptococcal organisms isolated from the feces of different animals, humans, water and sediments, we have attempted to correlate and match the gene fingerprints from the different sources. In this manner, we have attempted to establish the sources of, and thus the major contributors to, the overall bacterial pollution prevalent at the waterfront.

At present, the comparison and evaluation of differences and similarities in the hundreds of gene fingerprints studied to date has been performed manually by the investigators. We have tested a number of densitometric devices but their resolution capabilities are insufficient for distinguishing the multiple banding patterns obtained by gene fingerprinting. An alternative method has been studied which utilizes a system for automated computer-assisted analysis of gene fingerprinting data. We will describe a program that allows one to use a small computer equipped with a graphics tablet to scan a gene fingerprint by either wet-gel UV-illumination or white light illumination. The fingerprints are stored in a form in which they can be used later to compile similarities and differences as they relate to the different sources of the pollution.

Our manual results to date have indicated that gene fingerprinting is an extremely powerful tool that is only hampered by the time it takes to match and compare volumes of data over time. For example, geese contain many unique strains of fecal Streptococcal organisms, as determined by their unique gene fingerprints, although there are several "families" of these organisms which are extremely common among the geese populations. Furthermore, several of these common families are also present in water and sediment samples collected in and around the Western beaches area, suggesting that geese contribute significantly to the overall prevailing bacterial pollution. We are also developing DNA probes specific to the fecal Streptococcal organisms isolated from both human and non-human sources in order to provide a more sensitive, specific and rapid means of tracing sources and to quantitatively determine the total contribution of each source to the overall bacterial pollution present at the Toronto waterfront.

Fingerprinting the Toronto Waterfront: A Method for Tracing Fecal Bacteria to Their Source

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University of Toronto, Ontario Ministry of the Environment

Introduction

The closing of a number of Ontario beaches, in particular those in the Toronto area due to high levels of fecal bacterial indicators has led to legitimate concerns about the safety of swimming in these waters. Epidemiological studies have demonstrated that the occurrence of gastrointestinal illness among swimmers correlated with increased levels of indicator organisms (1). Such conditions obviously represent a significant health risk to any person bathing at these sites.

One major difficulty that has become increasingly evident in attempting to rectify the pollution problems in the Toronto area beaches has been the lack of methods for establishing the fecal sources of bacteria. Although human sewage has been blamed in part, the large colonies of ring-billed gulls and Canada Geese may also represent a significant source. Thus it remains a question whether the main source is human or non-human. In the present study we have used gene "fingerprinting" techniques (3-5) to examine fecal streptococci from goose droppings and water samples taken along the western beaches area of Toronto in order to ascertain its usefulness for tracing bacterial pollutants in the environment to their human or non-human source.

Materials and Methods

Bacteria. A total of 168 fecal streptoccoci were isolated from goose feces collected from different locations along the Toronto western beaches area (Figure 1). Isolations were performed according to the standard bacteriological methods recommended for these organisms (6). A selected number of these organisms were identified by the API system which indicated mainly *Streptococcal faecium* var. *casseliflavis* and *S. durans*, although in some cases not all isolates could be identified to species level. An additional 150 fecal streptococci were isolated from samples of surface water and water sediments (Figure 1). Other fecal streptococci, including *S. faecalis* var. *liquefaciens* and *S. faecium* from humans, and *S. faecalis* var. *liquefaciens* and *S. faecium* from gulls were also studied.

Chromosomal DNA preparation. Streptococcal chromosomal DNA was prepared as previously described (3).

Restriction enmdonuclease digestion of DNA. Approximately 1.0 to 2.0 ug of streptococcal DNA sample was used for each Hind III restriction endonuclease digest. The DNA was digested according to the supplier's specifications (Boehringer-Mannheim, St. Laurent, Quebec) except 10 to 20 U of enzyme were used per ug of DNA. Hind III recognizes a cleavage site sequence A↓AGCTT and was found to be suitable to produce highly resolved DNA restriction fragments from AT-rich streptococcal DNA.

Gel electrophoresis and photography. Sample preparation, the conditions of agarose gel electrophoresis and photography of the resultant Hind III restriction patterns were performed as previously described (3).

Cloning procedures. Streptococcal chromosomal DNA was purified and cloned into a pUC-9 plasmid vector according to the method previously described (9,10). The major advantage to using the pUC-9 system is that, insertion of streptococcal DNA into the multiple cloning site (MCS) of pUC-9, permits clones to be screened by a one-step assay that utilizes a simple histochemical reaction on agar plates. In this manner multiple "positive" clones containing streptococcal DNA can be assayed visually with relative ease.

Preparation of ^{32}P-labeled DNA probes. Duplex DNA samples were labeled with radioactive deoxynucleotide triphosphates by nick translation as previously described (4). The specific activities obtained were routinely 10^{8} cpm/ug of DNA. The labeled probes were used within one month of preparation.

Southern transfer and hybridization to ^{32}P-labeled probe DNA. Southern (8) blotting experiments were performed according to methods previously described (4).

Results

Restriction endonuclease analysis of goose fecal streptococci. In the first part of this study, the restriction endonuclease Hind III was used to digest 168 chromosomal DNAs of fecal streptococci isolated from goose feces collected at various location along the western beaches area of the Toronto waterfront (Figure 1). Agarose gel electrophoresis was used to visualize the resulting DNA fingerprints. Table 1 presents the number of Hind III patterns or fingerprints observed. A total of 19 sets of identical or very similar Hind III patterns were identified. Of these seven restriction patterns were observed more commonly, of which 19.6% (33 of 168) were of one type, designated as Hind III restriction pattern 1 (Table 1; Figure 3, lanes 5 to 8), 8.3% (14 of 168) were of Hind III pattern 2 (very similar to pattern 1) (Figure 3, lanes 9 to 12), 7.7% (13 of 168) were of Hind III pattern 3, 4.7% (8 of 168) were of Hind III pattern 4 and 5, and 2.3% (4 of 168) were of Hind III 6 and 7. Hind III patterns 8 to 19, comprised individually matched pairs each pair representing

1.2% (2/168) of the total fingerprints examined. In addition a total of 60 (35.7%) Hind III patterns could not be matched because of their distinct or unique pattern.

Restriction endonuclease analysis of water-borne fecal streptococci. The next part of the study was to compare the goose patterns observed with patterns observed from streptococci collected from surface water and water sediment samples. The main objective was to ascertain whether or not goose fecal patterns could be matched with the latter. Matching fingerprints in this manner would indicate that fecal material from geese finds its way into the watercourses.

Of the 150 samples analysed patterns from water sediment samples were matched with several goose patterns, including Hind III patterns 1, 2, 4 and 6 (Table 1). An example of this is illustrated in Figure 3. The water sediment patterns observed in lanes 2 to 4 are identical to the goose patterns 1 and 2 seen in lanes 5 to 8 and 9 to 12. Similarly, water sediment patterns observed in lanes 17 to 19 are very similar to goose pattern 6 seen in lanes 15 and 16. Goose pattern 6 was relatively common to patterns from water sediments (Table 1, patterns not shown). It was for this reason that this pattern (G-181) was chosen for cloning experiments. By contrast water surface patterns could not be matched to any of the characteristic goose patterns. It was apparent, however, that there were as many unique Hind III patterns as there were different streptococcal samples from both water sediment and surface water sources. An example of the unique patterns obtained is illustrated in Figure 3, lanes 1 to 8. Of particular interest was the observation that some patterns from isolates that could not be classified by API systems matched API classified streptococcal isolates (Figure 2, lanes 24 to 25). This suggested that the techniques could be used to classify unknown isolates to the species level.

Cloning goose fecal streptococcal DNA. Chromsomal DNA purified from isolate G-181, belonging to Hind III pattern 6 (Table 1) was used as the source DNA for cloning into the pUC-9 plasmid vector and propogation in *E. coli* strain JM103. The choice of G-181 was made because it was a pattern that appeared commonly among water sediment isolates. Furthermore its identification as a *S. durans*, a species that is relatively unique to geese (unpublished data), suggested it would be a promising candidate for developing a specific goose probe. Using the restriction enzyme Bam HI, a total of 72 streptococcal clones were obtained. Each clone contained a Bam HI fragment of G-181 streptococcal chromosomal DNA ranging in size from 1.5 Kilobase pairs (Kbp) to 11.1 Kbp (Figure 4).

Hybridization analysis of goose G-181 clones. Radioactive probes were made from human and gull fecal streptococcal DNA and hybridized to selected clones obtained from goose fecal streptococcal DNA G-181. Southern blotting analysis revealed that in each case the majority of the clones prepared did not hybridize. For example of 10 clones tested with the human probe only 2 reacted and of 15 clones tested with the gull probe again only 2 reacted. This indicated that of the 25 clones tested 21 appeared to be specific for the streptococcal DNA derived from goose fecal material.

Table 1. Hind III restriction patterns of chromosomal DNAs from goose fecal streptococci[g].

Hind III Restriction Pattern	No. Isolates	Percent %[a]
1	33	19.6
2[d]	14	8.3
3	13	7.7
4[e]	8	4.7
5	8	4.7
6[f]	4	2.3
7	4	2.3
8 - 19	(2)[b]	1.2
X[c]	60	35.7

[a] Total fecal streptococcal isolates examined = 168.

[b] 12 different pairs of Hind III patterns.

[c] X = all different or unique individual Hind III patterns.

[d] Very similar to Hind III restriction pattern 1. Both pattern 1 and 2 were observed in sediment samples.

[e] This pattern was observed in sediment samples.

[f] This pattern was observed in sediment samples and restriction fragments (G-181) were cloned into the plasmid vector pUC9 and reproduced in the _E. coli_ strain JM103.

[g] Mainly _Streptococcus faecium_ var. _casseliflavis_, and _S. durans_

Discussion

The ratio, Fecal Coliform:Fecal Streptococci (FC:FS), has been used as an indicator of human and non-human fecal sources. For example, the ratio in several major metro rivers has been recorded at less than 0.7 which suggested a non-human fecal source of bacteria, whereas the ratios from others have indicated a mixture of contamination (2). The large populations of ring-billed gulls and Canada Geese are thought to contribute significantly to these ratios but convincing evidence has not been forthcoming. Furthermore, the problem is also complicated by the fact that human sewage maybe also contributing to the indicator index. However, in light of recent evidence that the fecal flora of gulls and geese is not unlike that of humans (unpublished data), the reliability of these FC:FS ratios must be questioned. Thus there is an urgent need for a method that could specifically distinguish between fecal sources.

Restriction endonuclease analysis (REA) of an organism's DNA is a technique for uniquely identifying a bacterial isolate by its specific DNA pattern or gene "fingerprint." This technique offers considerable potential for use as an epidemiological tool for identifying sources and tracing routes of transmission of infectious agents, since it permits a direct approach to differentiating organisms regardless of whether or not identification or typing methods are available. For instance we have demonstrated the ability of REA to establish the epidemiological relationships between isolates of Campylobscter jejuni involved in cases of enteritis in a laboratory worker (5) and residents of of a boarding school (1). In each case REA could clearly distinguish between epidemiologically linked and unlinked C. jejuni isolates by agarose gel electrophoresis. We have also studied REA in combination with nucleic acid hybridization techniques (4). For example, specific DNA fragments may be identified by REA for their relationship to specific groups of organisms (11) or their association with a particular disease (12). These fragments may be extracted from gels, purified from other host cell sequences by molecular cloning and labeled for use as a probe.

The present study now extends these earlier observations to include the usefulness of these techniques as a means to trace environmental sources of pollution. Our REA of goose fecal streptococci have indicated that geese share many similar strains of bacterial organisms. We have seen this phenomenon in similar studies where chickens of the same flock share identical organisms (13). Preliminary REA of human and gull fecal streptococci have indicated similar results (unpublished data). Thus for each source there appears to be a distinct restriction pattern that could be utilized for determining the relative contribution of each to the over-all fecal pollution prevailing in environmental situations.

One practical problem associated with the use of REA in environmental applications is the large number of samples required for tracing a potentially large number of sources. At present we compare restriction patterns manually by eye. It is both time consuming and difficult to compare large numbers of patterns at one time. Automated and computerized systems such as the Eikonixscan 7800 (Eikonix Corporation) which is an image digitizer could be used for scanning and recording the differences and similarities in restriction patterns. Combined with programs such as are available for reading DNA sequence data from gels (14), a system for tracing sources could be readily established for handling large numbers of environmental samples.

Alternatively, REA combined with hybridization analysis could eventually identify specifically unique DNA sequences that could be prepared as probes. A DNA probe specific to human and non-human sources could then be used with rapid hybridization assays such as dot blotting in order to identify and quantitate the contribution of each source to the over-all bacterial pollution present in bathing water. A promising result of this study is the observation that unique clones can be prepared from goose fecal streptococci. These can be used as specific DNA probes for determining the degree to which Canada Geese contribute to the prevailing pollution. Our studies are continuing in this direction.

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Figures

Figure 1.

Locations of bacterial sampling along the Toronto western beaches area.

Figure 2.

Hind III restriction patterns of fecal streptococci from Canada Geese and water sediment samples. Lane 1: Lambda bacteriophage molecular weight markers; Lanes 2 to 4: water sediment patterns; Lanes 5 to 8: goose pattern 1; Lanes 9 to 12: goose pattern 2; Lanes 13 to 14: unique goose patterns; Lanes 15 to 16: goose pattern 6; Lanes 17 to 19: water sediment patterns; Lanes 20 - 23: similar sediment patterns; Lane 24: pattern obtained for *Streptococcus faecalis*; Lane 25: an unidentified fecal streptococci with an identical Hind III pattern as that seen in lane 24.

Figure 3.

Hind III patterns for fecal streptococci isolated from water sediment samples.

Figure 4.

Clones obtained from goose streptococcal strain G-181 (pattern 6). Panels (B) and (C) illustrate undigested clones; panels (A) and (D) are the digested (BAM HI) clones seen in panel (B) and (C), illustrating the various sizes of G-181 inserts present in the plasmid vector pUC-9 (represented by the common band as indicated by the arrows).

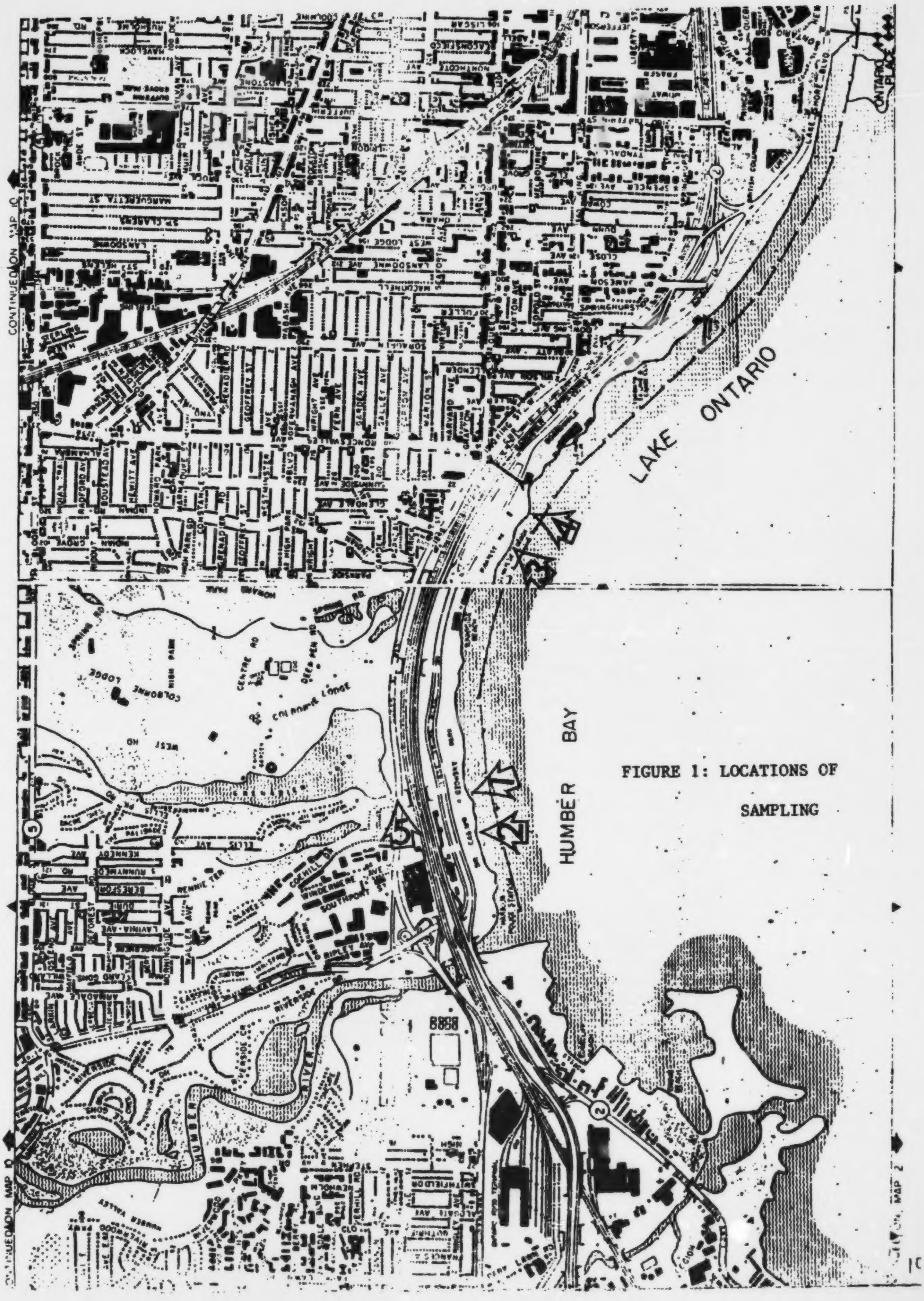
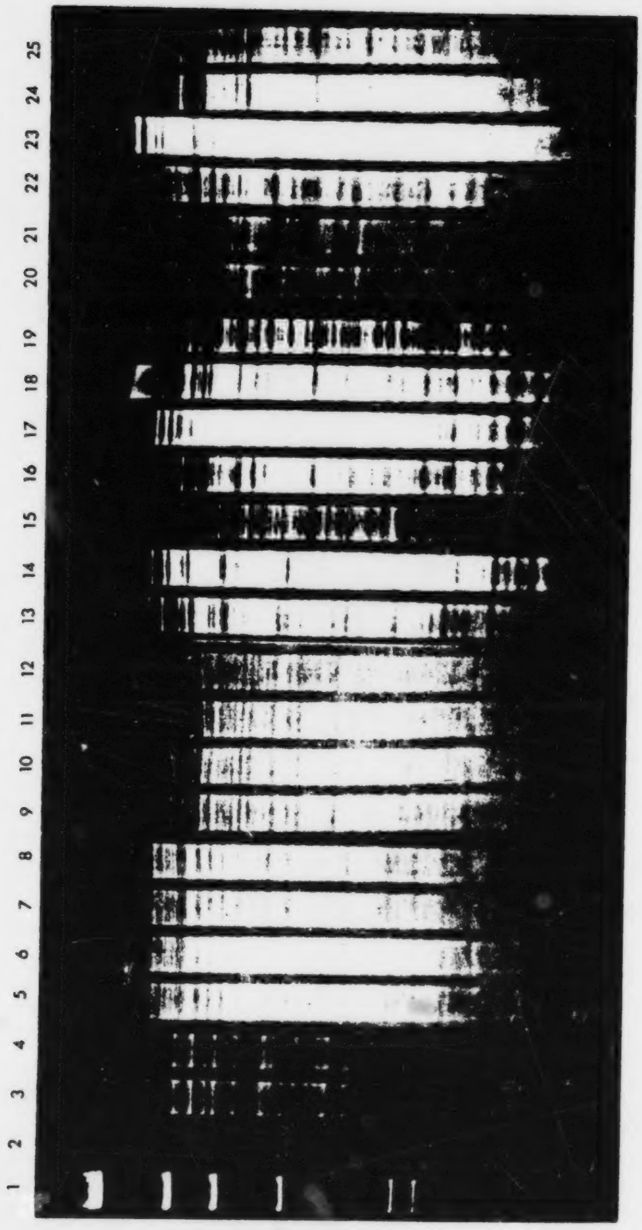

ONTARIO PLACE
LAKE ONTARIO
HUMBER BAY
HUMBER RIVER
1
2
3
4
5
CONTINUED ON MAP 10
CONTINUED ON MAP 2

FIGURE 1: LOCATIONS OF SAMPLING


1
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20
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FIGURE 2

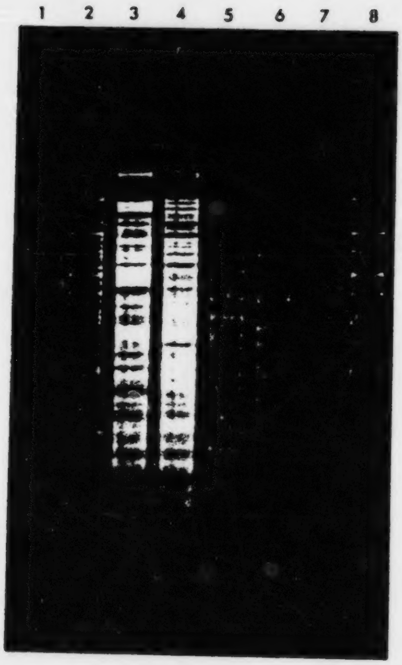

FIGURE 3

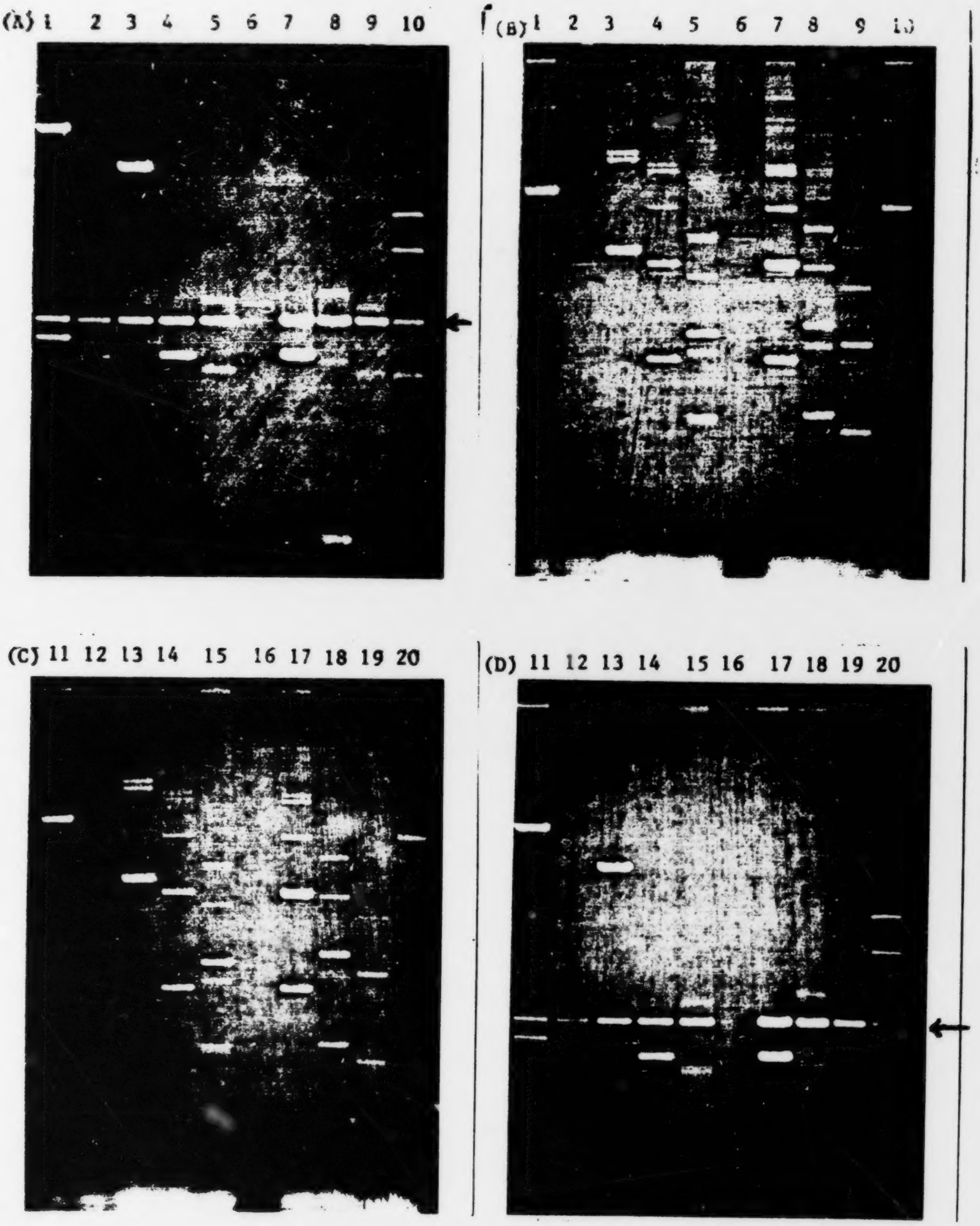
(A) 1 2 3 4 5 6 7 8 9 10
(B) 1 2 3 4 5 6 7 8 9 10
(C) 11 12 13 14 15 16 17 18 19 20
(D) 11 12 13 14 15 16 17 18 19 20

FIGURE 4

VALIDATION AND A POSSIBLE RE-ASSESSMENT OF CLAM CAGING EXPERIMENTS USING ELLIPTIO COMPLANATUS AS BIOMONITORS FOR TOXIC CONTAMINANTS IN WATER

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Key words: Clams, Biomonitoring, Toxic Contaminants, Bioaccumulation, Great Lakes.

ABSTRACT

A set of experiments was undertaken to examine the effects of cage design on the uptake and purging of toxic contaminants by the freshwater mussel Elliptio complanatus. Three types of enclosure apparatus were used to obtain comparisons of bioaccumulation rates at four Lake St. Clair sites, representing a wide range of toxicant levels (with respect to PCBs, OCS, lead and cadmium). The enclosures included wire cages (in standard use by MOE), circular corrals 1.25 m in diameter (each containing 5 clams) and clams, tethered to a transect with monofilament line. Another freshwater mussel, Lampsitis radiata siliquoidea, which is native to all Great Lakes, was compared to Elliptio by replicating each treatment.

The study clams were obtained from Balsam Lake, Rosedale, Ontario (for Elliptio) and Anchor Bay, Lake St. Clair (for Lampsilis). Clams and sediment samples were taken from each location where enclosures were deployed and from clam collection sites to determine background levels. The effect of sediment on toxicant uptake was examined using purified sand in half of the corrals.

The first set of clams was deployed in early June and recovered after a 46-day period. A second set of animals was deployed during the first week of September to make possible the examination of seasonal variation in contaminant uptake. Other aspects under study include sexual variation and the effect of varying exposure time on bioaccumulation of toxic contaminants by unionid molluscs.

Factors Influencing the Uptake of Toxic Contaminants by Unionid Molluscs

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Paul D. N. Hebert
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Abstract

Specimens of Lampsilis radiata siliquoidea and Elliptio Complanatus were transplanted from sites of low toxic contamination to four Lake St. Clair sites situated in and adjacent to a contaminant plume extending from the St. Clair River. Various enclosure apparatus were deployed in order to examine the effects of different confinement procedures on the acquisition of PCBs and octachlorostyrene by the two species. Exposure time versus toxicant uptake studies were performed to establish whether an asymptote is reached in contaminant levels or they increase infinitely. Preliminary results suggest that the enclosure type has little effect on contaminant uptake. Trends observed were similar for both species. Aroclor 1254 and octachlorostyrene levels in Lampsilis radiata siliquoidea appeared to reach a plateau after the initial exposure period (17 days).

Introduction

The ability of the soft tissue of lamillibranch molluscs to accumulate levels of toxic contaminants far in excess of those in the surrounding water or sediments has been well documented (Adams _et_ _al_., 1981, Foster and Bates, 1978, Hartley and Johnston, 1983). Experimental studies have indicated that these accumulations are primarily gained via exchange with the surrounding water mass (Pugsley _et_ _al_., 1985). Over the past decade it has become clear that analysis of these organisms can provide more detailed information of contaminant concentrations than studies which focus on sediment or water analysis. The usefulness of measurements of sediments is attenuated by the fact that the contaminants present in them may not be bioavailable, and because varying concentrations may reflect changes in the binding properties of the sediments rather than variation in contaminant levels in the water (McCrea _et_ _al_., 1985, Oliver, 1984). Direct analysis of water is made difficult since toxicant concentrations are often below the detection limit, and because pulsed or irregular discharges may go undetected (Kuntz and Chan, 1982). By contrast, contaminated levels in the body tissue of molluscs are likely to reflect concentrations integrated over a significant period of time. As a result of these advantages, molluscs have been widely used to monitor toxic contaminants (Greig and Sennefelder, 1985).

The first efforts employing molluscs to monitor contaminants in the Great Lakes involved the deployment of caged individuals of _Elliptio_ _complanatus_ at sites in the St. Clair, Detroit, and Niagara Rivers (Kauss _et_ _al_., 1981, Kauss _et_ _al_., 1985). In addition, Pugsley _et_ _al_. (1985) surveyed contaminant levels in natural populations of _Lampsilis_ _radiata_ throughout the Huron-Erie corridor. Kauss _et_ _al_. (1985) determined that there were releases of a number of organic contaminants along the Canadian shoreline of the St. Clair River and indicated that the water body showed little horizontal mixing. There thus appears to be a contaminant plume hugging the Canadian shoreline of the river. Analysis of natural mussel populations in Lake St. Clair provided further evidence of the discharge as plumes of both heavy metals and organic contaminants extended across the lake from the South Channel of the St. Clair River, suggesting that the contaminated water mass transversed Lake St. Clair with little mixing (Pugsley et al., 1985). Modelling studies also have indicated little horizontal mixing of water in the St. Clair River or of the river plume once it enters Lake St. Clair (Ibrahim and McCorquodale, 1985, Leach, 1980). As expected on the bases of past studies, the contaminant plumes in clams were far more distinct than those detected in sediments (Pugsley et al., 1985).

While these studies have demonstrated the usefulness of unionids in localizing the source and movement of contaminants, they are of less value in quantifying the amount of pollutant present. Little research has been aimed at determining the kinetics of the uptake process. Although it appears that contaminant levels reach an asymptote, it is not clear if the asymptotic concentration is linearly related to the mean concentration of the contaminant in the water. Furthermore, the amount of time required to reach this asymptote is uncertain. Past studies have suggested that the plateau for organics may be reached in a few weeks, and mussels used in monitoring studies are usually deployed for three weeks (Kauss et al., 1985). However, a comparison of levels in native clams and those in experimental animals indicated higher levels of octachlorostyrene in the native molluscs, suggesting that a longer exposure might lead to a further increase in contaminant levels. Additional complications arise from the need to confine mussels used in the experimental studies. Cage design may affect feeding behaviour and therefore have indirect effects on contaminant uptake (Adams et al., 1983). The present study has aimed both to examine the effects of different confinement procedures on contaminant acquisition by unionid molluscs and to compare the levels of toxicants accumulated by different freshwater mussel species when deployed on a transect that bisects the contaminant plume from the St. Clair River.

Methods

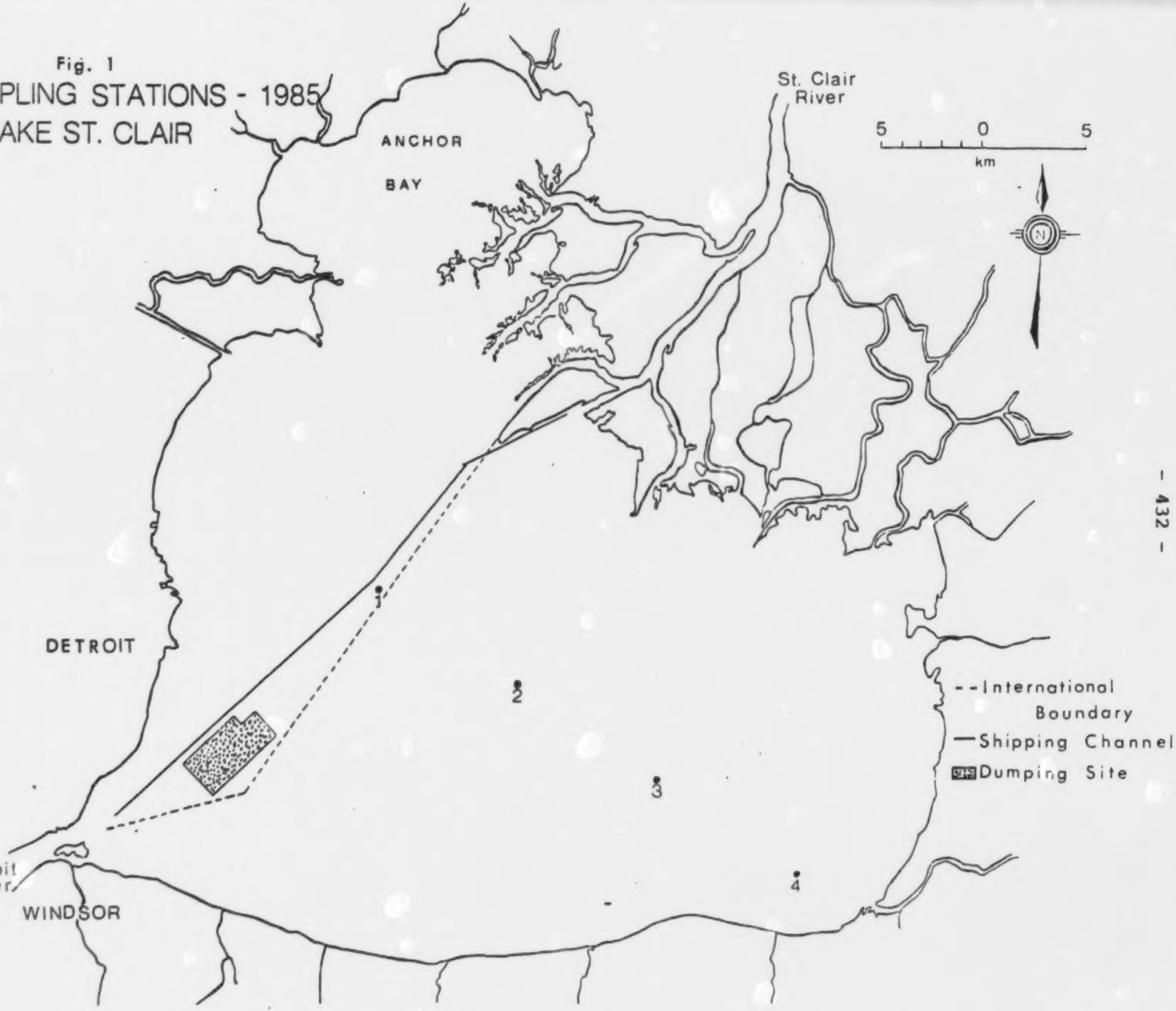
Clam collection and deployment

Four Lake St. Clair sites on a transect line crossing the contaminant plume were chosen for study (Fig. 1). The sites represented a wide range of toxicant levels with respect to PCBs, octachlorostyrene, lead and cadmium (Pugsley *et al*., 1985). Background levels of these contaminants and latitude-longitude co-ordinates for the sites are given by Pugsley *et al*. (1985) (corresponding site numbers are 69,25,16,11 for 1, 2, 3, and 4 respectively). Three types of containment apparatus were used: circular corrals, with an area of 0.47 m^2, were embedded into the sediment; galvanized wire-mesh 'pillow' cages, similar to those used by the Ministry of the Environment, were attached to a 1.5 m wire lead which was anchored to the substrate; and mussels were tethered to a transect with monofilament line. Five specimens of two unionid species, *Lampsilis radiata siliquoidea* and *Elliptio complanatus* were placed in each enclosure. At each site, four cages (two for each species) and four corrals (two with natural sediment and two with purified sand to examine the effect of sediment) were deployed. Hence there were no replicates for the corral treatments.

L. radiata is a native Lake St. Clair species that has a wide distribution in the lakes and rivers of southern Canada (Clarke, 1981). *E. complanatus* has been widely used by the Ministry of the Environment (Kauss *et al*., 1985), but is not native to the Huron-Erie corridor. To prevent accidental introduction, *E. complanatus* was not used in the leashing experiments. Mussels employed in the study were obtained from Balsam Lake, Rosedale, Ontario (for *E. complanatus*) and Anchor Bay, Lake St. Clair (for

Fig. 1

SAMPLING STATIONS - 1985
LAKE ST. CLAIR


St. Clair River
5
0
5
km
N
ANCHOR
BAY
DETROIT
1
2
3
4
- - International Boundary
—Shipping Channel
▨ Dumping Site
Detroit River
WINDSOR

L. radiata) and ranged in size from 6.5 to 7.2 cm and 6.5 to 7.5 cm respectively. Mussels (n=5) and sediment samples were collected from each site, including original collection locations, to determine background levels. The specimens were transported in bags of lake water maintained at 10° C and were deployed at the study sites within 36 hours of collection. L. radiata can be sexed using morphological variation (Kat, 1983), but gill structure must be examined microscopically to sex E. complanatus (Mackie, 1984).

An initial set of mussels were deployed for a 46 day period (June 6 to July 22, 1985). Difficulty was encountered in finding clam beds in Lake Huron; hence L. radiata specimens were taken from Anchor Bay. This resulted in a delay of 27 days in deployment and recovery of the L. radiata mussels. An entire second set of mussels were deployed on September 8 and removed on October 18, 1985. To study the effect of exposure time on toxicant uptake, L. radiata specimens (n=5) from Anchor Bay were placed in corrals with natural sediment at a polluted site (site 2) for periods of 17, 26, 46, and 87 days (July 22 to October 18, 1985). At the conclusion of the exposure period, individuals were immediately placed on ice, shucked within eight hours of collection, allowing excess fluid to be drained off, and wrapped in hexane-rinsed aluminum foil. Specimens were frozen(-20°C) until analysed.

Chemical analysis

All glassware employed was washed with hot, soapy water (Contrad 70, Canlab) and rinsed well with hot water. Immediately prior to use, glassware was rinsed three times with acetone, followed by three portions of petroleum ether, and a single rinse of pesticide grade hexane.

Whole mussel tissues were thawed, gill structure examined for sexing, and weighed. The tissue was placed in a glass beaker and homogenized in 120 mL of acetonitrile and 40 mL of deionized water using a Polytron for 90 seconds. The homogenate was filtered with suction through a sintered glass funnel, the homogenization was then repeated with 50 mL of acetonitrile, and finally the homogenate was rinsed with two 20 mL portions of acetonitrile. The combined homogenate was back-extracted with 300 mL of petroleum ether in three portions. The combined petroleum ether extracts were then washed with 200 mL water and dried by passage through columns containing 15 g of anhydrous sodium sulfate. The dried extracts were concentrated to 5 mL by air-drying and then put through a glass column containing 30 g of Florsil and 8 g of anhydrous sodium sulfate. The column was rinsed with 25 mL of petroleum ether followed by 25 mL of hexane, with the resulting elutant air-dried to 10 mL. A 1 uL sample of the elutant was injected into the gas chromatograph. Sediment samples will be analyzed following the procedure outlined by Pugsley et al. (1985).

Analysis was performed using a Hewlett-Packard Model 5790A capillary column GC-ECD fitted with a 15 m x 0.25 mm fused silica column, and auto-injector, and a Model 3390A (Hewlett-Packard) integrator. The following conditions for analysis were employed:

Injector temperature: 250° C
Column temperature programming: 0.5 min at 50° C, 50-250° C at 2° C min^{-1}, 30.0 min at 250° C
Detector temperature: 300° C
Detector make-up gas: 5% methane - 95% argon at 60 mL min^{-1}
Carrier gas: helium at 1.5 mL min^{-1}
Injection mode: splitless

Quantification of PCBs was performed using Aroclors 1242, 1254, 1260 as these are the congener groups most often found in environmental samples (Webb and McGath, 1973). For each Aroclor, only those peaks that represented greater than two percent of the total Aroclor area were used. This resulted in 17, 16 and 16 marker species for Aroclors 1242,1254, and 1260 respectively. The general equations used to quantify the three Aroclors are similar to those employed by Pugsley _et al_. (1985), with the exception that no response factor was included. Quantification of Octachlorostyrene (OCS) was performed by comparing peak areas against a set of standards containing OCS at known concentrations. The limits of quantification for OCS and PCBs were 0.02 ug L^{-1} and 0.1 ug L^{-1} respectively. The external standard method (one standard injected for every five samples) was used to determine recovery rates of 103 percent for Aroclor 1254, 109 percent for Aroclor 1260, and 85 percent for OCS. Reported values were not corrected to compensate for these recovery losses. Cleaning of glassware and purity of reagents were checked by analysis of blanks which had been submitted to the complete isolation procedure.

Results and Discussion

Both the cages and corrals proved to be effective enclosure apparatus for mussels. Overall, 311 of 320 animals deployed in the cages and corrals were retrieved. Only 50 percent of the leashed organisms were recovered, apparently due to the disintegration of the glue used to attach the line to the mussel shell.

Analysis of the mussels indicated the dominance of the Aroclors 1254 and 1260. Aroclor 1242 was not detected in any specimens or blanks. Solvent and method blanks yielded no detectable amounts of PCBs or OCS. Conversion of concentrations to dry weights for comparisons with the literature can be made using a multiplication factor of 6.667.

A preliminary estimate of contaminant levels in the various treatments was determined by analysis of single individuals from the autumn sampling at site 2, which lay in the plume radiating from the St. Clair River (Table 1). Analysis indicated the absence of Aroclor 1254 in the _E. complanatus_ mussels from Balsam Lake and low concentrations of Aroclor 1260 and OCS. The _L. radiata_ specimens from Anchor Bay showed low levels of both Aroclors and OCS. The two

Table 1. Concentrations (ug kg^{-1}) of PCBs (expressed as Aroclors 1254 and 1260) and Octachlorostyrene (OCS) in various treatments. Values expressed as wet weights

Treatment		Aroclor 1254	Aroclor 1260	OCS
E. complanatus	corral w/sediment	3.22	4.12	1.24
	corral w/sand	ND	4.81	3.83
	cage	9.09	4.39	11.83
	control-Balsam L.	TR	3.38	0.57
L. radiata	corral w/sediment	1.79	3.50	4.19
	corral w/sand	7.89	5.70	9.47
	cage	5.26	10.94	7.80
	leashed	6.67	4.37	4.53
	control-Anchor Bay	1.76	ND	1.56

ND-not detectable at applicable detection limit

TR-trace-under limit of quantification

Table 2. Concentrations (ug kg^{-1}) of PCBs (expressed as Aroclors 1254 and 1260) and Octachlorostyrene (OCS) in *L. radiata* mussels deployed in corrals for various exposure periods at site 2. Values are expressed as wet weights.

Exposure period (days)	Aroclor 1254	Aroclor 1260	OCS
17	7.58	0.47	6.61
26	4.57	10.35	7.57
46	ND	8.66	6.69
87	7.65	6.57	7.56

ND-not detectable at applicable detection limit species demonstrated the ability to bioaccumulate toxins when deployed at site 2, as evidenced by the up to 20 fold increase in contaminant levels. Differences between the species appeared to be small, as did the disimilarities among the four treatments. Clearly replicates are required in order that meaningful trends can be discerned. In general, specimens placed in purified sand had equal or greater toxicant levels than those deployed in corrals containing natural sediment. This suggests that the contaminants were derived from the water phase as oppose to the sediments.

Levels of PCBs and OCS obtained from L. radiata individuals were only slightly lower than those of native L. radiata specimens collected by Pugsley et al.(1985), suggesting a rapid approach to asymptotic values. This is supported by the exposure time versus contaminant uptake study which generally showed little increase in toxicant levels after the initial exposure period, with the exception of Aroclor 1260 which increased greatly after the first sampling and then stabilized (Table 2). Kauss et al.(1981) found organic contaminants to reach a maxium concentration after an exposure period of 8 to 16 days using E. complanatus as the biological monitor.

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REVISED MONITORING SCHEME FOR PERSISTENT AND TOXIC ORGANICS IN GREAT LAKES SPORTS FISH

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Key words: Toxic Organics, Great Lakes, Fish Analysis, Persistent Organics.

ABSTRACT

A monitoring program for the identification and quantification of semi-volatile, persistent and toxic organic contaminants has been undertaken on selected samples of sports fish from the Great Lakes. The analytical methodology employed cold acid dissolution of the tissue, partition of the organics into solvent, followed by Gel Permeation Chromatography for the removal of lipid materials, and finally, full scan gas chromatographic/mass spectrometric (GC/MS) analysis. In addition to this analysis, negative ion chemical ionization (NCI) GC/MS analyses were also performed to provide enhanced sensitivity for halogenated organics below the $\sim$50 ng/g (ppb) detection limit achievable by full scan electron impact GC/MS.

Samples of various fish species were collected from near-shore and open-lake areas of Lake Ontario, Lake Erie, Lake St. Clair, Lake Huron and Lake Superior. Summary data will be reported for the fifty samples analyzed and specific conclusions and recommendations based upon these data will be presented.

ABSTRACT

Based upon the literature review, a few methods were identified for the analysis of hazardous and persistent contaminants.

An evaluation of these methods was performed on laboratory fortified and naturally contaminated fish tissues. The fortification compounds were selected to encompass a full range of volatilities and acid:base characteristics. The methods tested included, cold acid dissolution with gel permeation chromatographic (GPC) clean-up, solvent homogenization with GPC clean-up and steam distillation. The test results revealed the latter technique was clearly inferior to the other techniques. The cold acid dissolution technique provided superior recovery to the solvent homogenization technique on most compounds tested. In addition, the acid digestion technique produced the highest residue concentrations for the naturally contaminated fish samples, thereby indicating greater extraction efficiency.

On the basis of these data, the cold acid digestion procedure followed by gel permeation chromatography for lipid removal was recommended for the monitoring of Great Lakes sport fish in Phase II of this project.

The monitoring program on fifty fish samples from five Great Lakes have revealed that the predominant contaminants present in the sports fish are currently covered by the Ministry's monitoring program.

Some additional contaminant groups were identified in many of these samples and evaluation for possible inclusion in the Ministry's routine testing program is recommended. These groups include chlorinated benzenes, substituted phenols, (particularly halogenated phenols), and polyaromatic hydrocarbons.

INTRODUCTION

In the process of attempting to monitor hazardous organic contaminants in sports fish from the Great Lakes, analytical chemists are faced with an extremely large array of hazardous compounds and possible analytical protocols. The number of possible permutations and combinations of chemicals and protocols is virtually unlimited, with only a very few of these combinations undergoing rigorous scientific testing such as a collaborative study. As the number of new and different chemicals enter the Great Lakes ecosystem (or as previously undetected chemical are identified) the array grows ever more confusing.

There are many of these chemicals which fortunately do not adversly affect the sport fishery either directly through fish health or reproduction or indirectly through bioaccumulation to concentrations adversely affecting their consumption. These chemicals due to their chemical nature undergo transformations that reduce their adverse effects on the sports fishery.

On the other hand, there are also some chemicals such as PCB, DDE and Mirex, which do adversely affect the Great Lakes sport fishery both directly and indirectly. These chemicals due to their nature tend to concentrate to significant levels in the fish tissues which are of concern for human consumption and also for species survival.

The objectives of this study were:

i) To review the recent literature on newly recognized hazardous organics with particular focus on the Great Lakes.

ii) To review the recent literature for the analytical protocols being used for the analysis of various substances in biological tissues, including fish, and to recommend those suitable for subsequent analysis of a limited number of whole-fish samples.

iii) To evaluate analytical protocols for their utility in screening Great lakes sports fish for hazardous and persistent chemicals.

iv) To identify and quantify the broadest possible range of organic contaminants in a wide range of fish species collected from all Canadian Great Lakes.

BACKGROUND

Contaminants In The Great Lakes Fish

Over the past two decades the number of detections of trace organic contaminants has been increasing considerably. These analysis have detected the presence of PCB, DDT and metabolites, chlordane, benzene hexachloride isomers including lindane, dieldin, endrin, chlorinated benzenes, mirex, mirex metabolites, and chlorinated styrenes (COA Report, 1981). The International Joint Commission has reported (Water Quality Board Report, 1978) in addition to the usual chlorinated hydrocarbons, the presence of phthalic acid esters, volatiles such as chloroform, bromoform and tetrachloroethylene, Toxaphene, polyaromatic hydrocarbons (PAH) and alkylated and chlorinated PAH and a broad array of aliphatic hydrocarbons (Hesselberg, 1982).

Numerous authors have more recently reported the presence of 2,3,7,8-tetrachlordibenzo-p-dioxin at part per trillion concentrations (Kiehl, 1981; Ryan, 1982; Harless, 1980). Additional analysis have also revealed the presence of ultra trace (part per trillion) levels of other chlorinated dioxins and polychlorinated-dibenzofurans (Keuhl, 1981).

Kuehl, 1980 has also reported the presence of hexachloro-and heptachoro-styrenes, pentachlorophenol and pentachlorobenzyl alcohol in fish samples in the Great Lakes watershed.

Chlorinated toluenes and chlorofluorotoluenes have been reported in fish tissue samples collected from the Niagara River (Yurawecz, 1979). Polychlorinated diphenyl ethers have been reported in sediments and fish collected from Whitby Harbour in Lake Ontario (Coburn, 1981) with levels higher than the PCB.

Polychlorinated naphthalenes have been detected and identified in fish from the Titabawassee River which flows into Saginaw Bay of Lake Huron (Kuehl, 1980) at very low parts per billion concentrations.

Hexachlorobutadiene and hexachlorocyclopentadiene have been reported to be in numerous hazardous waste landfills along the Niagara River in the New York State (Interagency Task Force on Hazardous Wastes, 1979) however only the hexachlorobutadiene was detected in the fish samples from the Niagara River (Yurawecz, 1979).

A comprehensive analysis of water and sediments adjacent to hazardous waste landfills in Niagara Falls, N.Y. (Elder, 1981) has detected chlorobenzenes, chlorotoluenes, polyaromatic hydrocarbons, PCB, chlorophenols, fluorinated aromatics, and a series of unchlorinated and chlorinated benzyl derivatives. There have been no reports in the literature of the detection of this latter group of organics in fish samples from Niagara River or Lake Ontario.

The report of Hesselberg (1982) also identified two halogenated contaminants found in Great Lakes fish samples which were not previously identified as pollutants of concern by the International Joint Commission. They were 3-chloro-1-propynyl-cyclohexane and 3-bromomethyl-cyclohexene with the latter compound being detected in all Great Lakes samples.

These reports reveal that as analytical techniques continue to improve, there are increasing detections of trace organic chemicals in the fish of the Great Lakes at ever lower concentrations.

ANALYTICAL METHODOLOGY ASSESSMENT

This review of the literature indicates that no universal extraction procedure exists when looking for the full range of contaminants in fish tissues.

The cold acid dissolution technique used by the Ministry of Environment compares favourably with other methods in terms of manpower and analysis costs. Those contaminants routinely analysed by this procedure are halogenated hydrocarbons and PCB's. This method reportedly offers good recoveries of these contaminants but requires judicious selection of aliquot size and clean up, particularly with high lipid content (>20%) samples. Another concern is the effect of low pH on acid sensitive pesticides such as dieldrin, and on basic compounds which will not extract from the HCl solution.

Steam distillation offers a good screening technique in qualitatively assessing many contaminants but reportedly does not produce quantitative recoveries for all halogenated hydrocarbons.

In the removal of lipids and the recovery of contaminants being analyzed, gel permeation has been shown to yield good recoveries of virtually all contaminant types and effective isolation from lipids.

Polytron homogenization (with dichloromethane) followed by GPC, permits the effective removal of lipid material by GPC and full scan GC/MS without significant lipid interference. The relatively clean extracts also will allow more specific techniques such as NCI to be used in detecting certain classes of contaminants.

GC/MS Conditions

Daily checks were performed on the GC/MS system to ensure good sensitivity and peak shape. Multiple standards were run to verify reproducibility of standard compounds. Any problems observed were generally gas chromatography related with higher molecular weight material condensing at the front end of the glass capillary column. When poor peak shape and/or sensitivity was observed a 0.5 to 1.0 meter section of the front end of the column was removed to improve chromatography. The GC/MS operating conditions were as follows:

Column - 30 m SE54 X 0.25 mm ID, 0.2 um film
Temp. Prog. - 70°C 2 min. - 280 @ 10° min.
hold 10 min.
Flow - 20 cm/min He
Injection Mode - Splitless, 1 min, injected @ 30 sec.
Split - 30 ml/min
Septum Sweep - 5 ml/min
Interface Direct couple, transfer line @ 250
Ionization Mode - Electron Impact
Electron Energy - 70 eV
Electron Multiplier 1150 V 1-5 X 10^6 gain
Scan - 100-550 AMU in 0.95 sec with bottom
hold .05 sec.
Ion Source - 170°

Quality Control

In the analysis of the real whole fish homogenates, isotopically labelled standards of d_{10}-anthracene and d_4 2-chlorophenol were spiked into the fish homogenates prior to the specific extraction procedure. Both surrogate standards were spiked at a total level of approximately 20 ug which corresponds to about 4 ppm for a five gram fish homogenate.

Samples

The "clean" whole fish homogenate used in the low and high level fortification study was a lake trout from Lake Opeongo in Algonquin Park. The "real" whole fish homogenate was a lake trout from North Shore, Lake Ontario. Lipid determination for these whole fish homogenates were 12.8 and 8.3% respectively. Equivalent blank whole fish homogenates were run in conjunction with each set of samples. Duplicate Gel permeation chromatography spikes of the fortified compounds were run to establish recovery from this analytical technique.

Fortification studies were done at the 100 ng and 20 ug per gram of whole fish homogenate.

Results and Discussion

The results of the fortification studies are presented in Tables 1 and 2. The polytron homogenization and cold acid dissolution techniques are clearly superior to the steam distillation technique.

The results from analysis of naturally contaminated tissue samples are shown in Tables 3 and 4.

These data reveal the superior performance of the cold acid dissolution procedure.

TABLE 1

RECOVERIES OF FORTIFIED COMPOUNDS

FOR LOW AND HIGH LEVEL SPIKING OF "CLEAN" FISH HOMOGENATE

MODEL COMPOUNDS	LOW LEVEL			HIGH LEVEL		
	Acid Digestion Recovery %	Polytron Homogenization Recovery %	Steam Distillation Recovery %	Acid Digestion Recovery %	Polytron Homogenization Recovery %	Steam Distillation Recovery %
Dichlorophenol	79.0	66.1	21.0	87.2	98.1	24.1
Trichlorophenol	78.3	63.0	-	78.9	64.3	-
Pentachlorophenol	105	100	-	81.7	40.0	-
Diphenyl Amine	-	36.5	47.0	-	83.8	14.0
Trichlorobenzene	90.7	74.4	49.0	76.6	83.8	61.4
Hexachlorobutadiene	64.7	68.6	40.0	70.1	83.3	62.6
Hexachlorobenzene	42.4	39.0	55.2	43.0	68.5	42.3
Mirex	36.8	44.7	4.5	83.1	94	3.5
p,p-DDE	*	*	*	94.7	93.0	9.9
Dieldrin	22.2	44.4	23.4	79.6	86.8	12.3
Fluoranthene	46.2	43.8	19.3	93.9	92.6	6.3
Phenanthrene d10	47.8	43.3	60.0	88.4	81.4	40.3

* High level in fish homogenate blank

TABLE 2

PCB RECOVERY

PCB Isomer	# of Isomers	Acid Digestion % Rec	Polytron Homogenization % Rec	Steam Distillation % Rec
Cl_2	3	74.3	65.5	91.8
Cl_3	4	85.4	70.5	73.1
Cl_4	4	93.5	85.7	35.9
Cl_5	5	94.0	92.7	19.3
Cl_6	6	102	103	4.7
Cl_7	4	103	103	-
Mean		92.0	86.7	37.5

Total PCB spike of 60 ug

TABLE 3

CONTAMINANTS IDENTIFIED IN REAL FISH HOMOGENATES BY GC/MS

(ng/gm)

CONTAMINANT	Mean Contaminant Concentration			Relative Recovery		
	Acid Digestion	Polytron Homogenization	Steam Distillation	Acid Digestion	Polytron Homogenization	Steam Distillation
Hexachlorobenzene	25.6	21.2	28.5	90	74	100
Pentachlorophenol	67.9	67.9	-	100	100	-
DDE	290	209	78.5	100	72	27
Octachlorostyrene	7.5	7.2	-	100	96	-
t-nonachlor	9.7	10.5	-	92	100	-
DDT	143	97.7	13.5	100	68	9
Mirex	37.0	33.9	10.2	100	92	28
Photomirex	8.7	8.8	2.5	99	100	28
Recovery (%)	Internal Standards					
D-10 Anthracene	111	110	90.1	100	99	81
D-4 Chlorophenol	41	5.4	35	100	13	85

TABLE 4

TOTAL PCB CONCENTRATIONS OF REAL FISH HOMOGENATES

Procedure	Mean Concentration (ug/g)
Steam Distillation	0.60 ± 0.07
Polytron Homogenization	0.80 ± 0.05
Acid Digestion	1.05 ± 0.06

MONITORING STUDY DESIGN

This monitoring study was designed to identify and quantify the broadest range of organic compounds possible. All samples were scanned to provide this information. Data presented in all tables reflect those chemicals which were found and not those which were sought.

All analytical techniques offer certain scopes with respect to sensitivity, selectivity, range of volatility etc. The cold acid dissolution technique was selected based on the best recovery of the contaminant types of concern in Great Lakes biota samples. The method was found to offer sensitivity for most compounds down to and below 50 ng/g. There are several exceptions to this detection level. PCB, Toxaphene, polychlorinated naphthalenes, polychlorinated terphenyls and polychlorinated diphenyl ethers are all comprised of large numbers of isomers (up to several hundred, in some cases). In these cases detection limits are much higher than for a single compound ranging from 500 - 2000 ng/g. Another factor which acts to elevate the achieveable detection limits is the greater MS fragmentation which occurs in some chemicals. PAH generally have little fragmentation and therefore have better sensitivity. On the other hand, compounds like Dieldrin fragment considerably using electron impact MS and therefore have poorer sensitivity.

Another scope limitation of the analytical method used in this study relates to the extract concentration used to achieve the nominal 50 ng/g detection limit. The evaporation of the solvent extract to a low final volume (20 ul) generally limits this analysis to chemicals with boiling points above 150°C. The analysis of more volatile organics would require a separate sample work-up which was beyond the scope of this study.

Also beyond the scope of this study, is the target analysis for polychlorinated dibenzo-p-dioxins (PCDD) and furans (PCDF). These contaminants must be analyzed using more elaborate clean up procedures and GC/MS conditions in order to achieve necessary sensitivity of 1 - 10 parts per trillion (pg/g).

Sampling Locations

This monitoring study was designed by officials of the Ministry of the Environment. The fundamental goal of the survey was to identify and quantitate the persistent and toxic organics in selected sport fish from all of the Canadian Great Lakes to ensure the Ministry programs continue to monitor those contaminants of concern. In addition to sampling open lakes locations, a number of samples were collected from near shore areas and harbours where the effects of urban and industrial discharges might be greater.

A total of twenty three (23) locations were sampled for this monitoring study.

Fish Species

A second consideration of the monitoring study was the species of fish analyzed. In the open lake locations, lake trout, siscowet, yellow perch, whitefish, splake, and channel catfish were the species selected for sampling. White sucker, long nose sucker, red horse sucker, white bass, and brown bullhead were selected as appropriate species for the nearshore and harbour sampling locations.

In all cases, whole fish samples were used for analysis. In some cases several samples were composited and then homogenized.

In order to minimize contaminant losses during storage, only fresh samples were supplied to ZENON for analysis and storage time prior to extraction and analysis was maintained at less than three weeks.

RESULTS AND DISCUSSION

Lake Ontario

Twenty samples were analyzed from Lake Ontario sites; four from open lake stations and sixteen from nearshore or harbour locations.

Analysis of six lake trout samples revealed high levels of PCB, p,p'-DDE, p,p'-DDT, chlordanes and Mirex. As shown in Table 5, these contaminants are included in the routine monitoring program performed by the Ontario Ministry of the Environment. Nonachlor (cis and trans) and photomirex were found around the 50 ng/g concentration level but are not included on the routinely monitored compounds list. Other compounds which were frequently detected, but at levels below 50 ng/g, were heptachlorostyrenes and octachlorostyrene.

Hexachlorobenzene was also present in all lake trout samples, usually below 25 ng/g. The other lower chlorinated benzene congeners were detected less frequently than hexachlorobenzene. Trichloro-, tetrachloro- and pentachloro-benzenes were found in a single lake trout sample from Port Weller. Dichlorobenzenes were found in five samples: two from Hamilton Harbour, one from Batchawana Bay, one from St. Lawrence River and one from Glenora. The concentrations of dichlorobenzenes in these samples ranged from 41. to 980 ng/g.

In addition to the standard full scan electron impact GC/MS analysis, selected samples were analyzed by negative ion chemical ionization (NCI) mass spectrometry. This latter technique provided significant sensitivity enhancement for many halogenated organics. Using NCI mass spectrometry, pentachloroanisole was detected in all

TABLE 5

LIST OF CONTAMINANTS ROUTINELY MONITORED BY ONTARIO MINISTRY OF THE ENVIRONMENT

Polychlorinated Biphenyls

Octachlorostyrene

p,p'-DDE

p,p'-DDD

p,p'-DDT

o,p'-DDT

Hexachlorobenzene

a-BHC

b-BHC

g-BHC

Aldrin

Heptachlor

a-Chlordane

g-Chlordane

Mirex

Toxaphene

three lake trout samples tested, where no sample analyzed by EI GC/MS detected pentachloranisole. Toxaphene was also detected using NCI, in the Port Weller lake trout sample and several isomers of polychlorinated diphenyl ethers were identified in the lake trout sample from near Burlington. The levels in these samples were not quantitated using the NCI technique, but are well below the 50 ng/g quantitation level set for this study.

In reviewing the data from other fish species from Lake Ontario chlorinated hydrocarbons and PCB similar to those discussed above were present and generally in the same relative proportions. There were some interesting differences found in comparing the white sucker and brown bullhead samples with the lake trout samples.

While only one lake trout sample (from Hamilton Harbour) contained any detectable level of polyaromatic hydrocarbons (phenanthrene, anthracene, and fluorene), every sample of sucker and bullhead from Lake Ontario contained polyaromatic hydrocarbons (PAH). The highest concentrations were found for phenanthrene, naphthalene, and fluoranthene while lower levels were found for pyrene, fluorene, and anthracene. No significant levels of alkylated PAH (which are indicative of petroleum PAH sources) were detected in these samples. The near shore sampling location for all of these samples may be the most important determinant in the finding of PAH.

One other interesting contaminant was detected in the sample of yellow perch from Jordan Harbour and in the brown bullhead sample from Hamilton Harbour. The compound was identified as a chlorotributyltin compound through library matching techniques. No authentic standard was analyzed to confirm this identity. The concentrations in these samples were estimated (using average response factors) to be 71 and 4 ng/g for the Jordan Harbour and Hamilton Harbor samples respectively.

Lake Erie and Lake St. Clair

Seven samples were analyzed from Lake Erie and Lake St. Clair. The only species analyzed were channel catfish, yellow perch and a sample of gizzard shad.

In general, the same chlorinated hydrocarbons and PCB were found in these samples as was found in the Lake Ontario samples. PCB, p,p'-DDE, and p,p'-DDT were found at the highest concentrations followed by the chlordanes and nonachlors. No Mirex, photomirex or chlorinated styrenes were detected in any of these samples.

The only sample found with polyaromatic hydrocarbons such as phenanthrene, fluoranthene, naphthalene, and pyrene was the channel catfish from Lake St. Clair. The levels detected were very low ranging from 0.3 - 4.6 ng/g.

One compound which was found in all samples from Lake Erie and Lake St. Clair (and in some Lake Ontario samples) remains unidentified. This compound shows an apparent molecular ion at m/z 180 and an intense fragment ion at m/z 137 (loss of 43). The base peak of the spectrum is m/z 124. The molecular ion and fragment ions all exhibit a small but significant $(m+2)^+$ ion; suggesting the presence of oxygen/sulphur.

Lake Huron

Twelve samples were analyzed from Lake Huron/Georgian Bay sites. These were comprised of single samples of lake trout, channel catfish, brown bullhead, and splake. In addition, two samples each of whitefish and white sucker along with four samples of yellow perch were analyzed.

Just as was seen in lakes Ontario and Erie, the predominant contaminants present in all samples were the PCB and DDT families followed closely by the chlordanes and nonachlors. Much lower amounts of hexachlorobenzene and alpha-BHC were found in most samples.

Some quite elevated levels of dichlorobenzene were found in the white sucker, brown bullhead and yellow perch samples collected from the North Channel area of Lake Huron. Lower Levels were present in two samples of Georgian Bay and Lake Huron whitefish. The four North Channel fish samples were also found to contain measureable levels of PAH with the sucker having generally higher levels than the perch and brown bullhead. No other samples from the Lake Huron sampling showed this range or these levels of PAH.

The contaminant (MW=180), which had been found in all other Great Lakes but had not been identified, was also found in one half of the samples from Lake Huron/Georgian Bay. It was not detected in the samples of lake trout, splake, brown bullheads or in the yellow perch from Georgian Bay.

Lake Superior

Eleven samples in total were analyzed from Lake Superior; six lake trout, two long nose suckers, two yellow perch, and one Siscowet.

As was found in all other lakes the lake trout samples from the open lake areas contained PCB and the DDT family in highest concentrations followed by the chlordane/nonachlor group and other chlorinated hydrocarbons including alpha-BHC, heptachlor epoxide, and dieldrin. The samples of lake trout from south east Lake Superior also contained a number of other halogenated organics identified as dichloroethylbenzene, bromochloroethylbenzene, bromoalkylbenzenes, dibromophenol tribromophenol, and trichlorophenol. In addition, a compound with an apparent molecular ion at m/z 190 and a two chlorine pattern was seen in all of these samples but remains unidentified.

Unlike the other fish species analyzed from Lake Superior, lake trout samples generally did not contain PAH. The exceptions were a lake trout sample from north-east Lake Superior which was found to contain 1 - 9 ng/g of several of the PAH and the siscowet. On the other hand, the yellow perch were found to contain from 8.5 - 40 ng/g of numerous PAH. The difference between these findings may reflect near shore versus open lake differences. The predominant PAH present were phenanthrene, fluorene, fluoranthene, acenaphthene, naphthalene, and pyrene. Very few alkylated polyaromatic hydrocarbons were detected in these samples indicating a combustion source rather than a petroleum source.

Dichlorobenzene was also found in only one sample yellow perch (north west Lake Superior). This finding, similar to the chlorinated benzenes around Hamilton Harbour and Bay of Quinte, may indicate the presence of localized point sources with subsequent contamination of the near shore species.

The sample of siscowet was the most highly contaminated sample analyzed from Lake Superior (consistent with a high lipid content). In addition to the commonly found chlorinated hydrocarbons and PCB, a high level of toxaphene were found using electron impact mass spectrometry. While the Toxaphene content was not quantitated because of differences in the ion series with those in the Toxaphene standard, the level was well above the 1-2 ppm detection limit achieveable using full scan EI GC/MS.

Using negative ion chemical ionization (NCI) mass spectrometry, toxaphene was also detected in some samples of lake trout.

CONCLUSIONS AND RECOMMENDATIONS

Fifty samples collected from twenty three locations in the Great Lakes were analyzed to identify and quantify persistent and toxic organics present.

The resulting data provide a window on each of the lakes for evaluating the adequacy of existing monitoring programs. The results from this limited study (in time and sample numbers) should not be interpreted to represent lake-wide contaminant levels. In addition these samples were all whole-fish samples, and were not edible portion samples which would be expected to contain lower contaminant levels.

A comparison of the compounds on the Ministry's routine sports fish monitoring program Table 5, with those contaminants detected in this study reveals that most of the higher concentration toxic organic contaminants present in the Great Lakes sports fish are currently being monitored.

There are however, some important exceptions. These exceptions fall into three main chemical groupings, namely chlorinated hydrocarbons, substituted phenols and polyaromatic hydrocarbons. The contaminants detected in the monitoring study which are not routinely monitored by the Ministry are presented in Table 6.

Within the chlorinated hydrocarbons, nonachlors and chlorobenzenes were frequently detected and in some cases at high (1-3 parts per million) concentrations. The other chlorinated hydrocarbons were generally at lower concentrations less frequently detected and partially addressed through the analysis of related compounds (ie. photomirex-mirex; heptachlorostyrene-octachlorostyrene).

TABLE 6 SUMMARY OF ADDITIONAL COMPOUNDS DETECTED BY GC/MS

CHEMICAL	SAMPLE DETECTIONS	# of LAKES
Naphthalene	20	5
Methyl naphthalene	5	2
Acenaphthylene	6	2
Acenaphthene	11	2
Fluorene	13	2
Phenanthrene	23	4
Anthracene	16	3
Fluoranthene	21	4
Pyrene	18	4
Chrysene	9	2
Benzanthracene	10	2
Benz(a)pyrene	4	2
Anthracenedione	1	1
Tris (Me-Et)Benzene	1	1
Methyldihydrofuranone	2	2
Dichlorobenzene	16	5
Trichlorobenzene	2	1
Tetrachlorobenzene	3	2
Pentachlorobenzene	2	1
Pentachloroanisole	5	2
Heptachlorostyrene	6	2
Photomirex	20	2
Dieldrin	22	4
Nonachlor	47	5
DDMU	17	3
Trichloroterphenyl	1	1
Tetrachloroterphenyl	2	1

CHEMICAL	SAMPLE DETECTIONS	# of LAKES
Unkn. Br(M.W.=134)	1	1
Unkn. Br(M.W.=136)	1	1
Unkn. Cl(M.W.=144)	5	3
Unkn. Cl2(M.W.=190)	10	4
Unkn. S (M.W.=180)	20	5
Benzoic acid	15	4
Benzene acetic acid	23	4
Benzene propionic acid	7	3
chlorotributyl tin	2	1
Methyl phenol	1	1
C2-Phenol	3	3
C3-Phenol	1	1
Dibromophenol	6	2
Tribromophenol	6	2
Trichlorophenol	3	1
CL7/CL8-diphenylether	1	1
C3-Benzaldehyde	2	1

No.of Lakes data includes Lake St. Clair

RECOMMENDATION

The Ministry should review the risk/hazard data available for the nonachlors and chlorinated benzenes with a view to extending the monitoring program to include these contaminants, particularly in near-shore sample collections.

The class of substituted phenols contained a number of different contaminants. Alkyl (two to nine carbons) phenols were found along with brominated and chlorinated phenols. Analysis of these contaminants is possible using the current MOE extraction technique but will required analysis additional to the standard electron capture gas chromatography. The technique which would permit the analysis of these contaminants at low levels in a single step is gas chromatography - mass selective detection (MSD). Using selected ion monitoring, sensitivities similar to those obtained on electron capture detection are readily obtained. This technique should be fully validated for the specific analyses prior to its use.

RECOMMENDATION

The Ministry should review the findings of substituted phenols, in particular of the halogenated phenols and assess these compounds for possible inclusion in the sports fish monitoring program.

The third major chemical class of concern is the polyaromatic hydrocarbons. These contaminants were detected in samples from all lakes and because of the carcinogenic properties of several members of this chemical class, they may represent a significant concern in sports fish. Based on the methodology evaluation phase of this study, the existing extraction protocol will also provide quantitative recovery of PAH. Two options exist for subsequent analysis of sample extracts, namely GC-photoionization detection (PID) and GC-MSD. The latter technique has the added benefit of also being capable of analyzing the substituted phenols.

RECOMMENDATION

Polyaromatic hydrocarbons should be reviewed for possible inclusion in the Ministry's routine monitoring program, particularly at the near shore locations. The PAH which should be reviewed for risk/hazard information, range from naphthalene to benz(a)pyrene.

A final consideration for the Great Lakes sport fish monitoring program is the inclusion of an element of chemical identification. The changes which occur over time and space suggest that a provision should be included in the monitoring program for on-going contaminant re-assessment. This may be done through the assessment of one lake each year or the testing of additional samples from near shore and open lakes areas. This testing will require the application of full scan GC/MS analysis to the sample extracts produced using the cold acid dissolution/GPC clean-up. In addition, where contaminants are of significant concern at concentration levels below the 50 ng/g full scan detection limit, some provision for target compound analysis using specific clean up or more sensitive MS analysis techniques should be incorporated into the monitoring program.

RECOMMENDATION

An ongoing organic contaminant identifications program should be incorporated into the Great Lakes Sports Fish monitoring program, along with a specific search for contaminants of concern at levels below the routinely achieved 50 ng/g full scan detection limits.

ACKNOWLEDGEMENT

The guidance, direction, assistance and review comments provided throughout this study by Mr. G.A.V. Rees and Mr. G. Crawford of the Ontario Ministry of the Environment are greatfully acknowledged. In addition, we wish to thank Mr. A.F. Johnson of the Ministry for his careful review and constructive suggestions. Finally we wish to thank Mr. D.M. Whittle, Department of Fisheries and Oceans, for his assistance in providing some of the test samples.

DEVELOPMENT OF A COST EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS OF TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGES AND FINAL EFFLUENTS

John Martin, Cecilia Chan and Dale Sutherland, Mann Testing Laboratories Ltd., and Gerry Rees and Tony Ho, Ministry of the Environment

Key words: Trace Organics, Sewage, Analytical Method, Effluent, Wastewater.

ABSTRACT

A novel analytical method has been developed for routine monitoring of trace organics in municipal wastewater. The prime objective of this work was to design a highly efficient protocol to ensure maximum sample throughput and to provide the required accuracy, sensitivity and reliability for such analyses.

Two methods were proposed and investigated in this study, which included the thermal stripping technique and the simultaneous in-situ acetylation and extraction method for bases, neutrals and phenolic compounds. The extraction performance was based on the results from a target list of chemical parameters chosen to represent various classes of compounds using organic free water, WPCP raw sewage and final effluents as test substrates.

The in-situ acetylation and extraction method was selected after preliminary investigation due to its ease of sample processing. The recoveries of the parameters and their corresponding coefficient of variation proved that the overall protocol was comparable, or in most cases, better than the EPA method 625. Some of the advantages of this method are:

- Rapid one-step extraction and derivatization
- No clean-up required
- Better recoveries for phenolic compounds and organochlorine pesticides
- Reduced fatty acid interference
- Better chromatography for phenolic and amino compounds.

All analyses were performed using a gas chromatograph coupled with a mass selective detector. Customized software was developed to generate multiple reports from a single analysis and to improve the autosequencing flexibility in sample processing and interpretation.

MOE PROJECT 96PL

Development of a Cost Effective Protocol for Routine Analysis of Trace Organic Contaminants in Municipal WPCP Raw Sewages and Final Effluents."

John Martin, Cecilia Chan and Dale Sutherland, Mann Testing Laboratories Ltd.

Gerry Rees and Tony Ho, MOE

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INTRODUCTION

The presence of a great variety of natural and synthetic chemicals in the sewage system is a known phenomenon. However, information on the composition, variability and fate of organic substances in the wastewaters was quite limited until the last decade. With the advance in modern technologies, substantial research efforts have been directed to analyze wastewater and to assess the potential chemical threats posed by the systematic discharge of wastes into the environment.

Several major studies have been conducted in both Canada and the Unites States in recent years. For example, in 1978, the United States Environmental Protection Agency conducted a full scale study to investigate the occurrence and fate of the 129 priority pollutants in the 40 publicly owned treatment works(1). In the same period, another study was funded by the EPA to develop analytical methods for the analysis of raw wastewater and sludge samples and to obtain information on the priority pollutants in a number of treatment plants throughout the nation(2). In Canada, a similar survey was also conducted by the Ontario Ministry of the Environment and the Environmental Protection Service of Environment Canada to identify and quantify the organic compounds in nine treatment plant effluents in southern Ontario(3). A review of the data, generated by the Ministry of the Environment, indicates that the potential health hazards of prime concern include a group of 22 specific compounds. These compounds were emphasized due to their biological accumulation potential, persistence, frequency of occurrence and mean rank concentrations.

Due to the complexity of the matrix, complicated extraction and cleanup procedures are usually required. The analytical protocol generally involves three analyses per sample (volatile, acid and base/neutral fractions). These procedures greatly increase the cost of analysis and are therefore not ideal for high volume routine screening purpose. To address this problem a study was commissioned in 1984 by the Ministry of Environment to develop a cost effective protocol for the routine analysis of trace organic contaminants in Municipal Water Pollution Control Plants raw sewages and final effluents.

A novel analytical method was developed from this commissioned study. The method ensures maximum sample throughput and provides the required accuracy, sensitivity and reliability for such analysis. Customized software was also developed to assist sample processing and data interpretation.

This paper discusses the preliminary results of this project. Also discussed is the automation aspect of the analytical protocol which plays a significant role in increasing throughput and reducing the cost of analysis.

BACKGROUND

The development of wastewater analytical methods for efficient sample processing has always been a continual challenge. The vast array of organics present at low concentrations (less than 10 ug/L) in municipal wastewater requires complicated extraction, isolation and detection procedures. Added to this is the fact that large amounts of interferences are usually present in the extracts, consequently requiring extensive cleanup procedures.

In 1979, the US EPA published a series of procedures for the analysis of the 129 priority pollutants in wastewater(4). These procedures include (a) 12 methods for gas-liquid and high performance liquid chromatography with specific detectors and (b) 3 methods using gas chromatography/mass spectrometry for multiple measurements. Because of the high complexity of the organic contaminants in wastewaters, GC/MS methods are usually the methods of choice in most analyses. Method 625 is a general screening method for priority pollutants, which consists of a base/neutral extraction followed by an acid extraction. This method, while very useful for most applications, suffers from some drawbacks. The initial base/neutral extraction may cause significant reduced recoveries of phenol, 2-methyl phenol and 2,4-dimethylphenol. The bases such as benzidene and other amines are difficult to chromatograph. In addition, presence of fatty acids in wastewater would result in a very complex chromatograms.

Another approach was funded by the USEPA to modify and develop an analytical approach to enable the analysis of raw wastewater and sludge samples. Results of this study were detailed in a report submitted to the EPA by F.P. DeWalle and E.S.K. Chian(5). The analytical method used in this study involved an acid/neutral extraction followed by a base extraction. Due to the high concentrations of organic interferences in this type of samples, special separation and cleanup procedures such as gel permeation chromatograhy, florisil chromatography and cesium silicate chromatography were required to facilitate analysis for individual group of compounds. This method produced a base fraction, 3 neutral fractions and 1 acid fraction which was derivatized with diazomethane.

The results of this study indicated detection limits of about 1 ug/L for the extractable organics and 5-10 ug/L in sludge samples. Although this method offers cleaner fractions for processing, there are several drawbacks that discourage its use for routine monitoring. Firstly, the procedure is time-consuming and labor intensive and consequently reduces sample throughput. Secondly, the multi-fraction approach results in more losses of organics due to the separation processes. Thirdly, the cost of analysis will be very high as it involve a minimum of three extractable fractions and one volatile fraction.

Macroreticular resins such as XAD have been used successfully in a number of studies to absorb organics from water. This technique has proven to be very effective in removing organics from water (6-8) and is a useful method in concentrating organics with no emulsion problem.

Recently, bonded phase silica adsorbents such as Bond-Elut cartridges have also been used for the specific adsorption of organics. However, due to the low loading capacity of the cartridge, 150 ml of water is usually the maximum volume that can be extracted without evidence of breakthrough.

While there are advantages in using these adsorption methods, application to municipal wastewater analysis does not seem to be practical. Since municipal raw sewages and final effluents usually contain high levels of suspended solids, elution through the adsorption bed would easily be interrupted by the fine particles clogging the passage. Furthermore, preparation of scrupulously clean adsorbents is usually lengthy, thus reducing the processing advantage of the technique.

Other techniques for extraction and concentration of organics in water such as close-loop stripping, steam distillation and reverse osmosis have also been considered. However, they either lack universality for broad screening purposes or are very time-consuming and would not be suitable for this project.

To achieve the project objectives, two novel approaches are used in this study : a) simultaneous in-situ acetylation and extraction followed by the purge and trap method and b) a thermal stripping method. These methods are initially investigated to select the best approach for this project.

Since free fatty acids are known to be one of the major classes of interferences in wastewater, a critical aspect in this study is the ability to separate the fatty acids from compounds of interest without using elaborate cleanup steps. The proposed in-situ acetylation method offers a solution to this problem and yet still maintains a high sample throughput.

This technique involves the addition of methylene chloride, potassium bicarbonate and acetic anhydride to the water sample. Under the basic pH, the neutral and basic compounds are extracted into the methylene chloride layer. The phenolic compounds are converted by acetic anhydride to their respective acetates while the amines are converted to their corresponding amides. These derivatized products will then be easily extracted into the methylene chloride layer. Since the acids themselves are not derivatized by the acetic anhydride, they will remain in the aqueous layer.

Using this method, all bases, neutrals and phenols can be extracted in one fraction , the overall recoveries of phenolics will greatly be increased because of the single extraction. The fatty acids stay in the aqueous layer, producing a cleaner extract for chromatographic analysis.

The other method, thermal stripping, allows both volatile and non-volatile organics to be stripped out of water and collected in a sorbent tube. Subsequent thermal desorption of the sorbent tube enables all organics to be analyzed in this step, thus greatly reducing the number of analyses per sample.

EXPERIMENTAL

SIMULTANEOUS IN-SITU ACETYLATION AND EXTRACTION

All raw sewage and final effluent samples were collected from Main Treatment Plant in Toronto and provided by the Water Resources Branch of the Ministry of the Environment. A 500 ml sample of wastewater was accurately measured and fortified with several labelled standards to monitor the extraction efficiency.

A 150 ml aliquot of methylene chloride was added to the sample bottle and mixed thoroughly for 10 minutes on a magnetic stirrer. Approximate 10g of anhydrous $KHCO_3$ was then added and stirred for another 5 minutes to ensure complete dissolution of the solid. An accurately measured 2.5 ml of acetic anhydride was finally added to the bottle and vigorously stirred for an hour. At the end of the extraction, the two phases were allowed to separate in a separatory funnel and the organic layer collected in a round bottom flask. When necessary, the samples were subjected to centrifugation to break the emulsions. The extractive acetylation was repeated twice with 50 ml of CH_2CL_2 and 15 minutes of stirring each time. The methylene chloride layers were then combined, passed through pre-washed sodium sulfate, and concentrated to about 2-3 ml. The extract was further concentrated to 1 ml with a gentle stream of nitrogen and spiked with a internal standard prior to autosampler processing.

THERMAL STRIPPING TECHNIQUE

All analyses were carried out using a Dynamic Thermal Stripper (Envirochem. Inc.). This instrument contained a heated sparging unit with a temperature control module. In addition, the sparging unit provided two flow paths with adjustable rates. One was used to purge the sample, the other entered downstream of the sample to provide an additional flow of dry gas to increase the ability of the gas stream to hold the water vapour as it passed through the sorbent tube. The organics purged out of the water sample were collected on a multi-layer sorbent tube directly above the sparger. A maximum of three water samples could be processed simultaneouly to increase the throughput.

A 30 ml aliquot of the water sample was transferred to the sparging vial and purged with helium at 85°C for 40 minutes at a flow of 100 ml/min. The organics stripped out of the water were collected on a sorbent tube containing glass beads, tenax, ambersorb 340 and charcoal which was maintained at 70°C with a secondary gas flow of 80 ml/min to dry the tube. At the end of the purging cycle, an addition 5 minutes of secondary helium flow was allowed to pass through the sorbent tube to ensure all the water vapor had been purged out of the system. The sorbent tube was then thermally desorbed using an UNACON concentrator and the organics analyzed by GC/MS.

INSTRUMENTATION

Analysis of the extractable organics was performed on a Hewlett Packard Mass Selective Detector system interfaced with a HP 5890 gas chromatograph. Chromatographic separation was achieved with a J & W DB-5 fused silica capillary column (30 m x 0.25mm, 0.25um film thickness). The chromatographic conditions were as follows: Injector temperature, 250°C; temperature program,70°C hold for 1 min, 20°C/min to 170°C , 5°C/min to 200°C, 20°C/min to 280°C with a final hold of 12 minutes. The interface temperature was 285°C. The linear velocity of the helium carrier gas was 30 cm/sec. Samples were introduced in the splitless mode with the solvent vent closed for 0.5 min after injection.

Mass detector conditions were as follows: electron energy, 70eV; MS operating mode, SIM; Dwell time per ion, 100 msec. Electron impact spectral data was acquired and processed by the HP 9816 computer and the corresponding MSD software.

Volatile organics and the sorbent tube samples were analysed on a UNACON 810B automatic concentrator (Envirochem Inc.). This instrument was equipped with a sparging assembly for analysis of volatile organics in water, and a desorber unit for thermal desorption of the sorbent tubes. The internal trapping system consisted of a large bore primary trap which permitted preliminary separation of compounds of interest from the carrier gas. The secondary small bore trap was approximately one-tenth the capacity of the first trap and allowed for an efficient transfer of the retained compounds to the capillary column.

Initial concentrator operating conditions were: transfer line to MS, 280°C; valve compartment, 250°c; trap 1 desorbed at 300°C with a helium flow of 50ml/min for 5 minutes; trap 2 desorbed at 300°C with a helium flow of 3 ml/min for 5 minutes onto a 30 m DB-5 column.

For volatile organics, a 30 ml aliquot of the water sample was transferred to a 50 ml sparging vial and purged for 15 minutes at a flow rate of 50 ml/min at 50°C. For sorbent tube analysis, the tube was placed inside a desorber unit with both ends tightly sealed by vespel/graphite ferrules. The sorbent tube was then rapidly heated to 300°C with a helium flow of 50 ml/min for 15 minutes to release the organics into the first trap. By sequential heating of the first and second trap, a discrete narrow-band plug of sample was deposited on the head of the column.

RESULTS AND DISCUSSION

EXRACTION METHOD

Preliminary investigation of the recoveries of selected organics using the in-situ acetylation and extraction technique have been conducted in final effluent, raw sewage and reagent water matrices. Results of these analyses are presented in Tables I to III and the corresponding chromatograms in both Scan and SIM modes are shown in Figure 1a),1b) and 1c) respectively. Figure 2 shows a normalized comparison of Final Effluent and Raw Sewage chromatograms.

The Ontario Ministry of the Environment has preliminary identified more than 84 compounds for this study. Based on the frequency of occurrence and concentration levels of organics reported in the previous studies (1-3), a short list containing the most frequently detected organic priority pollutants in municipal wastewaters are summarized in Table VI. A target list was then generated to represent a broad spectrum of organics and used throughout this study to test the protocols. These target compounds were:

Halogenated Aliphatics
Chloroform
Dichlorobromomethane
Tetrachloroethylene
Trichloroethylene
1,1,1-Trichloroethane
Vinyl Chloride

Halogenated Aromatics
Chlorobenzene
Hexachlorobenzene
1,4-Dichlorobenzene
Aroclor 1254

Non-Halogenated Aromatics
Benzene
Benzo(a)pyrene
Chrysene
Dibenzo(a,h)anthracene
Naphthalene
Styrene

Miscellaneus
Dimethyl Disulphide
1,4-Dioxane

Pesticides
Diedrin
gamma-BHC
Diazinon
p,p'-DDT
Chlordane
Atrazine

Phenols
Phenol
Pentachlorophenol
o-Cresol
2,4,6-Trichlorophenol

Phthalate Esters
Bis(ethylhexyl)phthalate

Amines
Aniline

Ethers
Diethyl Ether

Initial extraction using 500 ml of organic free water indicates good recoveries for phenolic compounds which range

TABLE I

RECOVERIES OF THE TARGET ORGANICS IN REAGENT WATER

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	8.82	10.7	86.0
Aniline(A)	15.00	14.06	9.7	93.7
O-Cresol(A)	10.58	12.09	8.8	94.9
Napthalene	10.18	9.31	15.4	91.5
2,4,6 TCP(A)	9.94	9.12	5.5	91.7
HCB	10.10	9.03	5.4	89.4
Atrazine	11.26	10.76	2.5	95.6
Gamma-BHC	17.00	17.80	2.9	104.7
Diazinon	21.50	19.31	4.4	89.8
Pentachlorophenol(A)	9.94	7.93	9.7	79.8
Alpha-Chlordane	12.70	11.82	8.0	93.1
Dieldrin	10.12	9.37	5.4	92.6
4,4'-DDT	10.06	9.37	3.8	96.7
Chrysene	22.50	21.94	8.5	97.5
Bis(Ethyl-Hexyl)Phthalate	10.32	7.63	6.0	74.0
Benzo(A)Pyrene	10.20	8.98	7.1	88.0
Dibenzo(A,H)Anthracene	21.20	19.52	6.1	92.1

(A) = Acetylated

TABLE II

RECOVERIES OF THE TARGET ORGANICS IN FINAL EFFLUENT

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	7.75	7.2	75.5
Aniline(A)	15.00	14.42	13.5	96.1
O-Cresol(A)	10.58	11.07	24.5	104.6
Napthalene	10.18	9.03	7.8	91.0
2,4,6 TCP(A)	9.94	8.47	4.4	91.0
HCB	10.10	9.60	3.7	95.0
Atrazine	11.26	9.20	9.8	81.7
Gamma-BHC	17.00	16.28	5.2	95.8
Diazinon	21.50	18.14	7.2	84.4
Pentachlorophenol(A)	9.94	8.58	4.3	88.3
Alpha-Chlordane	12.70	9.16	4.5	72.1
Dieldrin	10.12	8.69	3.5	85.8
4,4'-DDT	10.06	11.43	16.17	94.4
Chrysene	22.50	16.41	2.2	72.9
Bis(Ethyl-Hexyl)Phthalate	10.32	7.76	12.9	75.7
Benzo(A)Pyrene	10.20	9.43	6.5	92.5
Dibenzo(A,H)Anthracene	21.20	20.41	7.5	96.3

(A) = Acetylated

TABLE III

RECOVERIES OF THE TARGET ORGANICS IN RAW SEWAGE

PARAMETER	SPIKED LEVEL (ng)	MEAN LEVEL DETECTED (ng)	% CV	MEAN % REC
Phenol(A)	10.26	7.52	6.0	73.3
Aniline(A)	15.00	13.39	6.1	89.3
O-Cresol(A)	10.58	7.66	9.6	72.4
Napthalene	10.18	8.92	6.5	87.6
2,4,6 TCP(A)	9.94	9.09	2.7	91.4
HCB	10.10	10.80	2.8	106.9
Atrazine	11.26	11.18	17.1	99.3
Gamma-BHC	17.00	13.85	9.1	81.5
Diazinon	21.50	22.28	3.6	103.6
Pentachlorophenol(A)	9.94	8.73	9.8	87.8
Alpha-Chlordane	12.70	10.20	9.9	80.3
Dieldrin	10.12	6.92	6.0	68.4
4,4'-DDT	10.06	7.98	7.9	79.3
Chrysene	22.50	16.86	7.0	74.9
Bis(Ethyl-Hexyl)Phthalate	10.32	10.68	14.2	103.5
Benzo(A)Pyrene	10.20	10.31	11.3	101.0
Dibenzo(A,H)Anthracene	21.20	19.30	4.6	91.0

(A) = Acetylated

FIGURE 1a)

Final Effluent Chromatograms

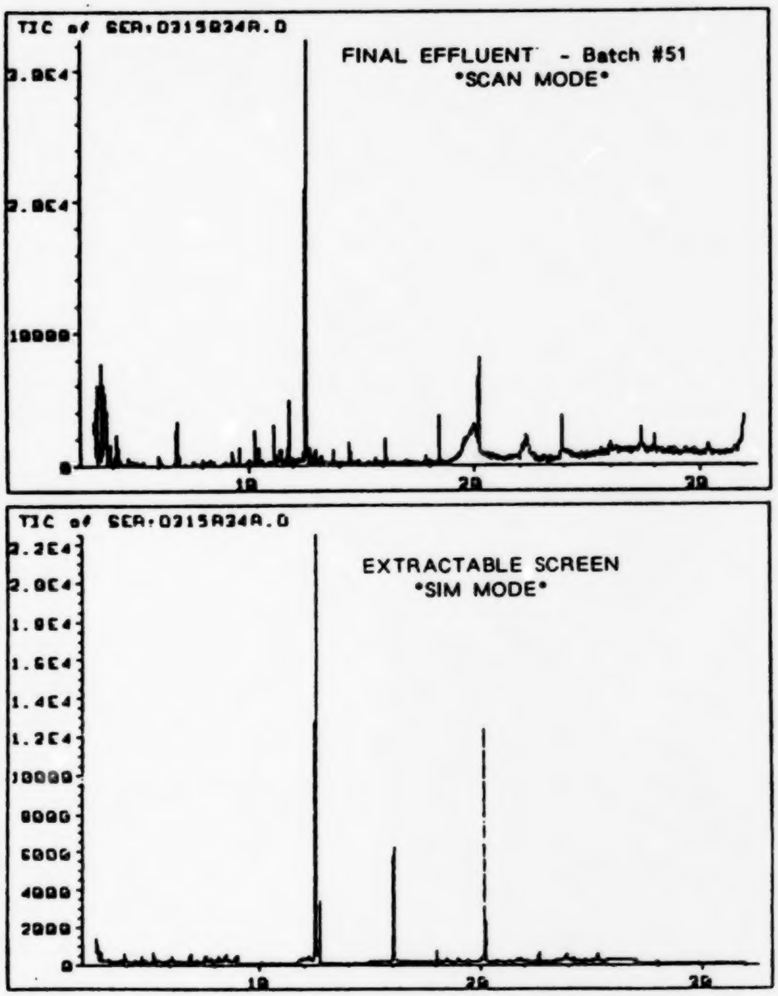


Figure 1b)

Raw Sewage Chromatograms

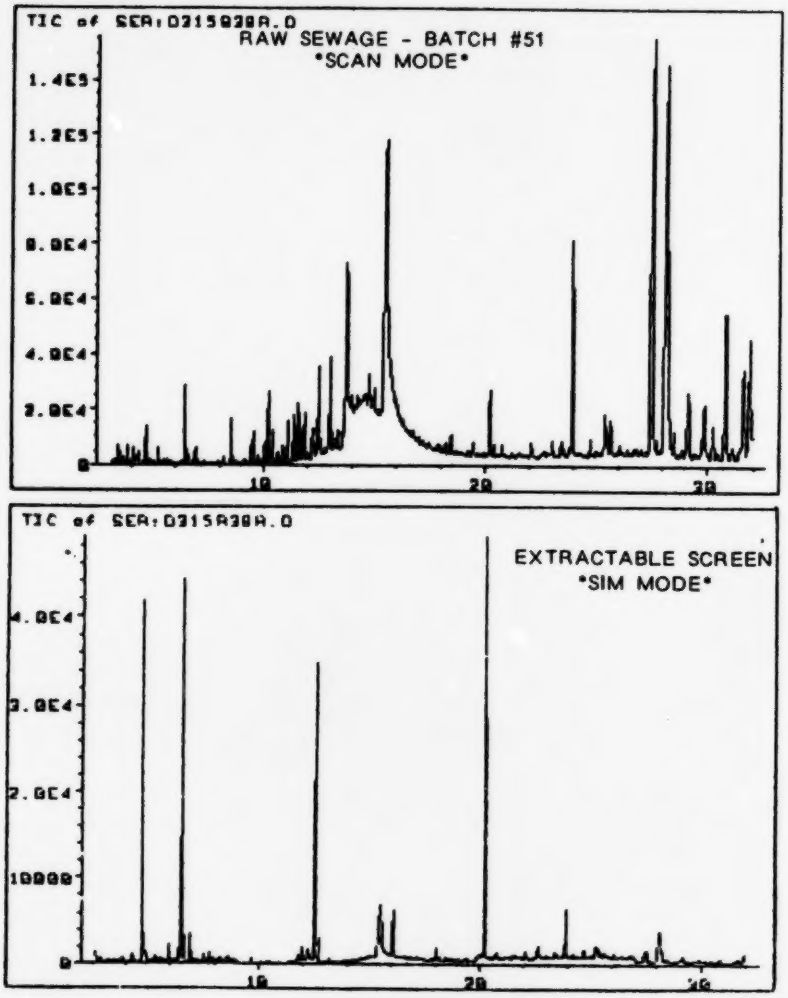


Figure 1c)

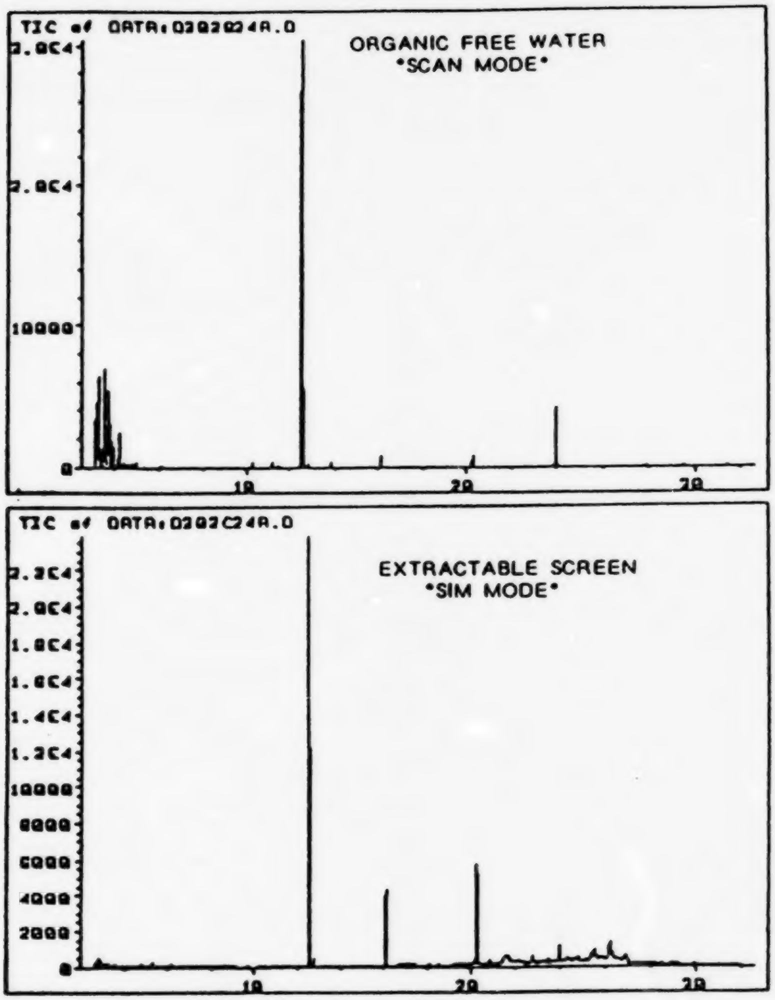
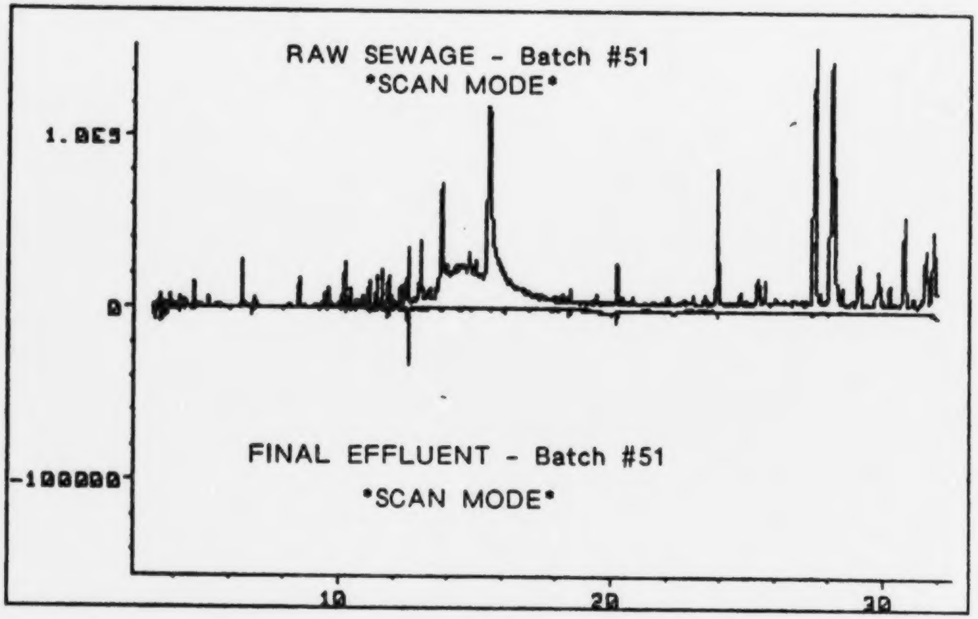

TIC of DATA:0202024A.D
ORGANIC FREE WATER
•SCAN MODE•
3.0E4
2.0E4
10000
0
10
20
30
TIC of DATA:0202C24A.D
EXTRACTABLE SCREEN
•SIM MODE•
2.2E4
2.0E4
1.8E4
1.6E4
1.4E4
1.2E4
10000
8000
6000
4000
2000
0
10
20
30

Figure 2

Sample Chromatograms Comparisons: normalized for the ISTD's



from 80% for pentachlorophenol to 94% for o-cresol. These recoveries are far better than those of EPA method 625 due to the fact that the phenols were extracted and derivatized in the same fraction, thus eliminating losses in the initial base/-neutral fraction. In addition to the phenols, amines were also converted to amides which greatly improved the chromatography and ultimately the sensitivity.

The recoveries of the phenols were calculated based on those obtained from the repective standards under the same conditions as detailed in the experimental section. The quality of the data will not be affected since both standards and samples were treated the same.

It is well known in the EPA method 625 that some organochlorine pesticides such as alpha and beta BHC, endosulfan I and II and endrin are subject to decomposition under the alkaline conditions of the extraction step. By using this in-situ acetylation method in which a weaker base such as potassium bicarbonate was used, the recoveries and reproducibility of these compounds were found to improve significantly.

The isolation and identification of trace hazardous organics from complex background is the prime aim of any wastewater extraction procedure. In most methods used today, gel permeation chromatography or other column cleanup procedures are frequently employed to reduce interferences, thus resulting longer sample processing time. Using this in-situ acetylation method, the fatty acids which are present at high concentrations in municipal wastewater would not be derivatized and would remain in the aqueous layer therefore greatly reducing the chromatographic background and eliminate the need for a cleanup step. On the other hand, by eliminating the acid compounds, the phenoxy herbicides which contain the carboxylic acid functional group would not be detected.

Using this approach, all bases, neutrals and phenols will be extracted in the same fraction. Hence, only one extractable and one volatile fraction are needed for each sample. With autosamplers for sample introduction, coupled with extensive

TABLE VI

Most Frequently Detected Organic Priority Pollutants in Influent and Effluent Samples

	% Occurrence				
	Influent (ug/L)			Effluent (ug/L)	
Compound	Study #1	Study #2	Study #3	Study #1	Study #2
Methylene Chloride	83	92	-	79	86
Chloroform	74	91	100	55	82
1,1,1-Trichloroethane	90	85	72	53	52
Trichloroethylene	90	90	65	67	45
Tetrachloroethylene	94	95	100	77	79
1,4-Dichlorobenzene	83	-	50	38	-
Ethyl Benzene	87	80	50	13	24
Toluene	84	96	86	45	53
Phenol	86	79	72	38	29
Naphthalene	86	49	-	24	6
Phenanthrene	57	20	17	15	3
Diethyl Phthalate	91	53	-	62	13
Di-n-butyl Phthalate	89	64	28	85	52
Bis(2-Ethyl hexyl) Phthalate	86	92	-	76	84
Butyl Benzyl Phthalate	77	57	-	32	52
1,2-trans-Dichloroethylene	-	62	-	-	13

software development for data processing, a high sample throughput with minimum manpower requirement can be achieved.

VOLATILE ORGANIC ANALYSIS

In combination with the in-situ acetylation method, a capillary purge and trap method was used for the analysis of the volatile organics. Depending on the sample volume, this technique can be used to produce sub-ppb detection limits for a large number of volatile compounds.

Table V Mean % Recoveries of Volatile Organics Using Purge and Trap Method

Compound	Mean Recovery (%)	C.V. (%)
Vinyl Chloride	93.9	10.3
Chlorofrom	81.2	3.6
1,1,1-Trichloroethane	102.5	9.5
Benzene	91.4	7.2
Bromodichloroethane	96.0	4.9
Trichloroethylene	91.1	7.4
Tetrachloroethylene	80.3	7.6
Chlorobenzene	78.5	5.4
Diethyl Ether	66.4	9.7
Dimethyl Disulphide	80.0	7.9
Styrene	91.1	9.2
1,4-Dioxane	0.3	8.5

The purging efficiency and reproducibility of the target compounds are depicted in Table V. The purging efficiency is a reflection of the percentage of the amount of a specific compound that can be recovered from water. In these analyses, the accuracy of the results was not be affected by the low recoveries since samples and standards were analysed using the same procedures.

In this study, it was observed that the recovery of 1,4-Dioxane was extremely poor. This was mainly due to the misicibility of this compound with water. With an increase in temperature during sparging and a higher ratio of gas flow verus sample size, a better recovery was obtained. Recoveries of the other volatile compounds were very good. They ranged from 66% for diethyl ether to 102% for 1,1,1-Trichloroethane. The coefficient of variation for majority of the compounds were well within 10%.

THERMAL STRIPPING TECHNIQUE

Analysis of water samples for intermediate to high molecular weight organics using closed loop stripping and steam distillation techniques have been effectively demonstrated in the past years (9,10). The purge and trap method (11) has also been used to analyze semi-volatile organics. Some of the reasons prohibiting this technique from analyzing higher molecular weight compounds were the condensation of organics in the sparging vessel and the large amount of water vapor retained in the trap.

To solve these problems, Envirochem Inc. (Klemblesville, Penn.) has designed a stripping unit which is able to sweep both the volatile and non-volatile organics out of the water. The design of this unit is detailed in the experimental section.

Initial investigation of this technique revealed that most of the organics could be purged out of the water and trapped in a sorbent tube. This tube contained glass beads, tenax, ambersorb 340 and charcoal to extend the trapping capabilities. Presented in Table V are the recoveries of selected organics. One interesting observation is noted in the water misicible compounds. The recoveries of aniline and p-dioxane which were extremely low using the purge and trap method were found to be over 70% using the thermal stripping technique. These results indicates that elevated temperature and a high carrier gas flow will improve the purging efficiency of the organics.

Table IV Mean % Recoveries of the Target Organics Using Thermal Stripping Method

Compound	Mean Recovery (%)	C.V.(%)
Vinyl Chloride	85.8	7.3
Chlorofrom	73.0	13.2
1,1,1-Trichloroethane	92.5	7.3
Benzene	95.1	16.2
Bromodichloroethane	81.1	24.7
Trichloroethylene	86.3	14.2
Tetrachloroethylene	74.3	10.3
Chlorobenzene	74.8	18.8
Diethyl Ether	85.7	27.8
Dimethyl Disulphide	78.5	23.8
Styrene	67.8	11.8
1,4-Dioxane	70.0	15.6
Aniline	79.2	18.4
Phenol	79.0	23.7
o-Cresol	101.8	10.7
Naphthalene	94.0	10.8
2,4,5-Trichlorophenol	ND	-
alpha-BHC	90.7	20.5
Hexachlorobenzene	84.3	42.5
Atrazine	ND	-
gamma-BHC	60.2	25.8
Diazinon	110.6	11.0
Pentachlorophenol	ND	-
alpha-Chlordane	114.9	6.0
Dieldrin	112.0	12.4
4,4'-DDT	ND	-
Chrysene	ND	-
Bis(2-ethylhexyl)phthalate	ND	-
Benzo(a)pyrene	ND	-
Dibenzo(a,h)anthracene	ND	-

Application of this technique to PAH and phenol analysis was not very sucessful. The PAH's required reasonable temperature for proper desorption which could have caused thermal degradation of the heat labile compounds. The phenols were not detected partly due to the difficulty in chromatographing these compounds without derivatization.

This technique shows promise in the field of trace organic analysis since the entire sample would be analysed and sensitivity would no longer be a problem. A cleanup step would not be required using this method. However, extensive development will be needed to allow for reliable monitoring.

DETECTION SYSTEM

Element specific detectors and multi-column chromatographic systems have been used extensively in many applications as a means of identification and quantification of the organic compounds of interest. However, when dealing with complex matrix such as municipal wastewater, the multi-column and multi-detector approach is not adequate for reliable identification. For example, Figure 7 shows a sediment extract which was previously sujected to florisil column cleaup and analysed by a dual column dual ECD system. Since the sample contained a high concentration of polychlorinated biphenyls, several pesticides that eluted in the same fraction could not be identified due to interferences from the PCB peaks. The same sample was also injected into a GC/MS system and the ions of interest were extracted. Figure 8 illustrates the p,p'-DDE peak detected in the same sample. From this result, it is clear that GC/MS is a better choice for this type of analysis. The main drawback of using this instrument is its high cost and the expertise required in the operation and interpretation of the results.

A recent breakthrough in gas chromatographic detection system is the modification of the full size mass spectrometer into the small inexpensive desk top detector which maintains most

Figure 7

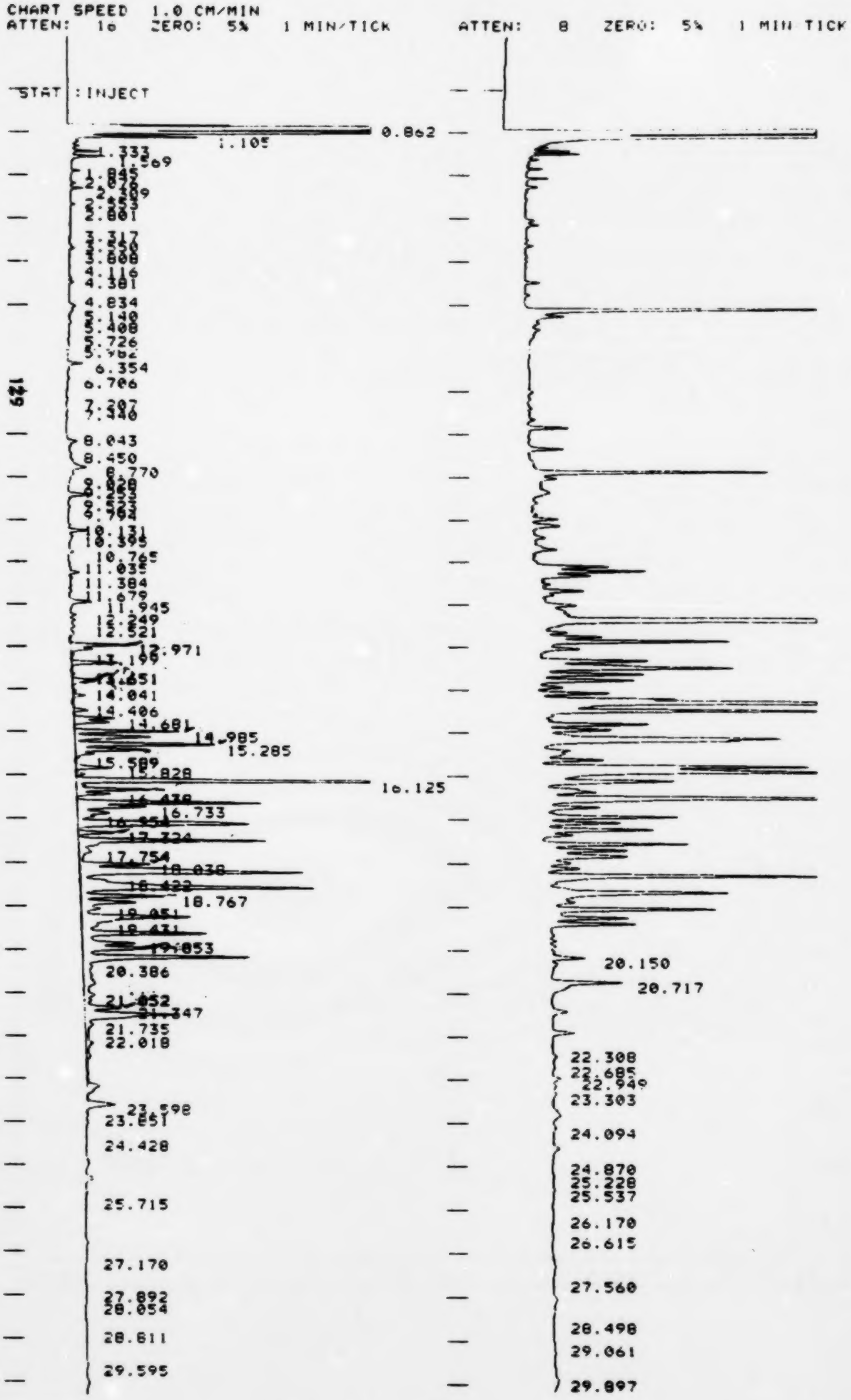
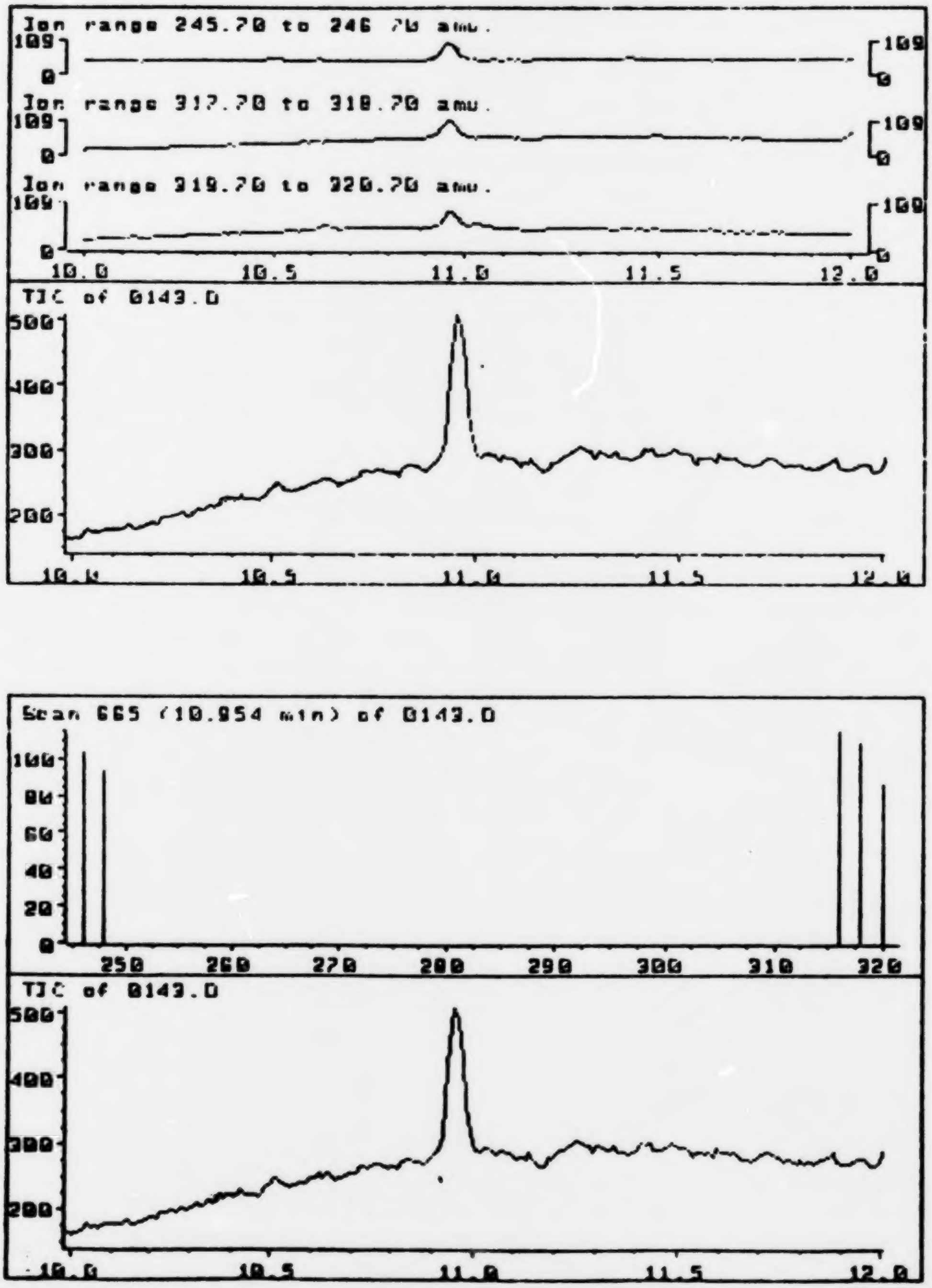


CHART SPEED 1.0 CM/MIN
ATTEN: 16 ZERO: 5% 1 MIN/TICK
ATTEN: 8 ZERO: 5% 1 MIN TICK
START
INJECT
0.862
1.105
1.333
1.569
1.845
2.076
2.309
2.553
2.801
3.317
3.550
3.808
4.116
4.381
4.834
5.140
5.408
5.726
5.962
6.354
6.706
7.207
7.346
8.043
8.450
8.770
9.020
9.253
9.523
9.764
10.131
10.395
10.765
11.035
11.384
11.679
11.945
12.249
12.521
12.971
13.199
13.651
14.041
14.406
14.681
14.985
15.285
15.589
15.828
16.125
16.438
16.733
16.954
17.324
17.754
18.038
18.422
18.767
19.051
19.431
19.853
20.386
21.052
21.347
21.735
22.018
23.598
23.651
24.428
25.715
27.170
27.892
28.054
28.811
29.595
20.150
20.717
22.308
22.685
22.949
23.303
24.094
24.870
25.228
25.537
26.170
26.615
27.560
28.498
29.061
29.897
129

Figure 8


Ion range 245.70 to 246.70 amu.
100
0
100
0
Ion range 317.70 to 318.70 amu.
100
0
100
0
Ion range 319.70 to 320.70 amu.
100
0
100
0
10.0
10.5
11.0
11.5
12.0
TIC of 0143.D
500
400
300
200
10.0
10.5
11.0
11.5
12.0
Scan 665 (10.954 min) of 0143.D
100
80
60
40
20
0
250
260
270
280
290
300
310
320
TIC of 0143.D
500
400
300
200
10.0
10.5
11.0
11.5
12.0

of the capabilities of the mass spectrometer but with fewer options. This type of detector can be operated in the single ion mode which is similiar to a conventional GC detector.

In this project, a Hewlett Packard mass selective detector was used. Customized software was developed to allow unattended sample handling and data processing.

This detector was exclusively used in the "Selected Ion Monitoring" mode to obtain the best possible sensitivity, improved quantitation and increase computer storage capability. The sensitivity of the SIM mode (10-100pg) was sufficient to detect concentrations of organics found in raw sewage or final effluent.The readily detectable limits of 100 pg for most of the hazardous organics enabled only 500 ml of sample to be routinely processed.

For each parameter in the target list, three ions were selected based on their intensity and uniqueness. To confirm the identity, retention times and the ratio of the two qualifying ions to the quantition ion had to be within the strictest tolerence. Two time reference peaks were chosen to help define the relative time window for each parameter. Internal standard quantitation method was used in these analyses.

For Aroclor 1254, a quantitation ion was selected from each of trichloro, tetrachloro, pentachloro and hexachloro cogener groups, these, coupled with the two qualifying ions and scanning over the entire range of the expected retention times, provided positive confirmation of the presence of Aroclor 1254. Quantition was achieved by the summation of these target peaks.

SOFTWARE APPROACH

Automation is becoming an important aspect in most analytical chemistry laboratories. There are obvious reasons for increasing automation such as : less time is spent in sample introduction and repetitive laboratory endeavour; greater standardization of data collection and reduction operations results; more attention is paid to problem solving; and flexibility is increased.

In order to assure the accuracy of the detection and maximum efficiency for sample processing and interpretation, extensive software development was required. Our major objective in this regard was to effectively identify and quantify the compounds of interest under various adverse chromatographic conditions such as background interference, overloading and saturation problems which commonly occur in this type of analysis.

Software development from these concerns resulted in the creation of a series of independent programs. These programs were developed to ease the process of data reduction and achieve a high level of automaticity. Furthermore, they can either be linked together or processed individually. Typical examples of some of the programs are:

- a program to extract and integrate ions of interest and to display the information in a way which is easily witnessed by the operator (Figure 3)
- a program to detect the overloading and saturated peaks
- a program to provide spectra of each peak in the chromatogram (Figure 4)
- a program to automatically initiate and set up an autosequencing method
- the "Mann Link", a top view type program that adds a new dimension to autosequencing capability and flexibility (Figure 5)
- a full and sophisticated background substracted spectra library search program
- a program that allows a visual pattern recognition format for Aroclor 1254 (Figure 6)
- a program to conduct daily QA/QC and compare previous results automatically

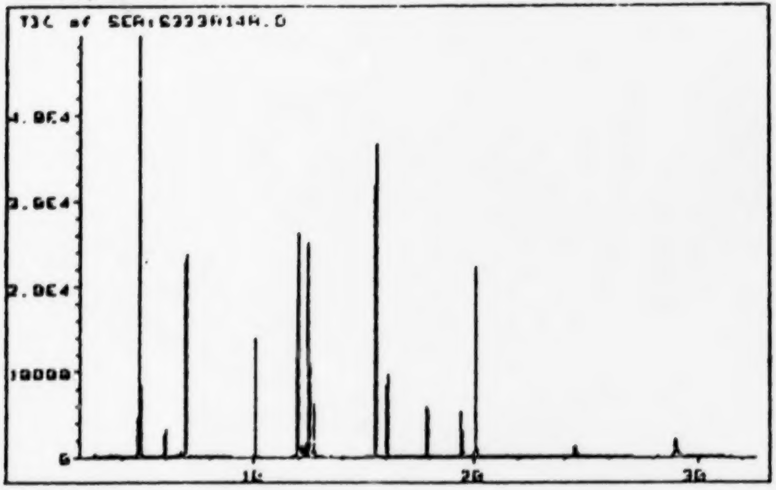
Following each acquisition, data reduction macros were used to display the three ions for each compound, and to monitor the quality of the integration. Separate tests were automatically run to flag any saturated or overloading peaks. Subsequent internal standard reports were processed and automatically printed.

Peak identification in the report program had to meet the

Figure 3:

Data Processing: an example;

```
Data file: SEA:S333A14A.D
 File type: GC / MS DATA FILE

 Name Info: STANDARD #62B        X10L  *MOLSIM.M*
 Misc Info:
 Operator : DS

 Date      : [illegible]    [illegible] pm
 Instrument: MS 5970
 Inlet     : GC

 Sequence index :    1
 Als bottle num :   14
 Replicate num  :    1
```



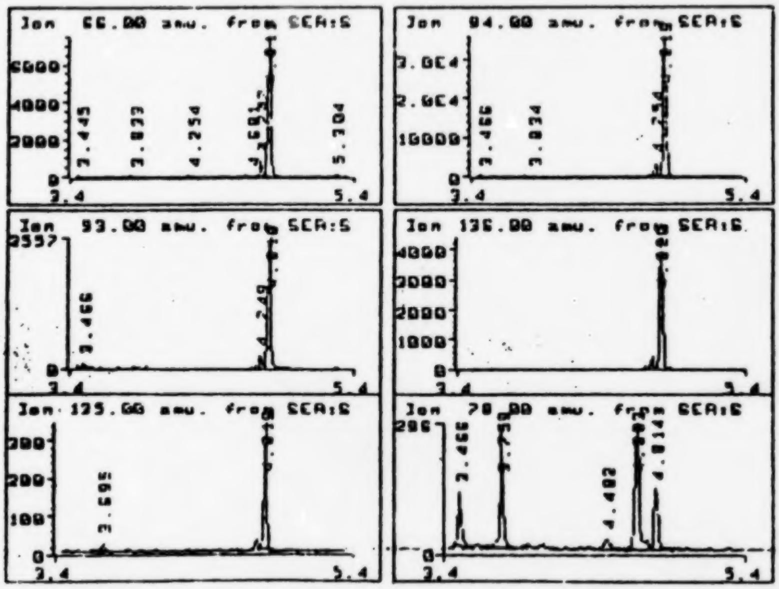
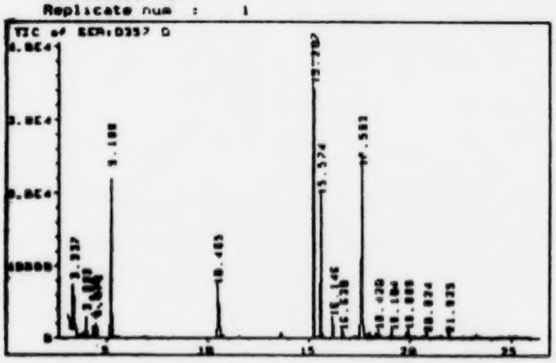
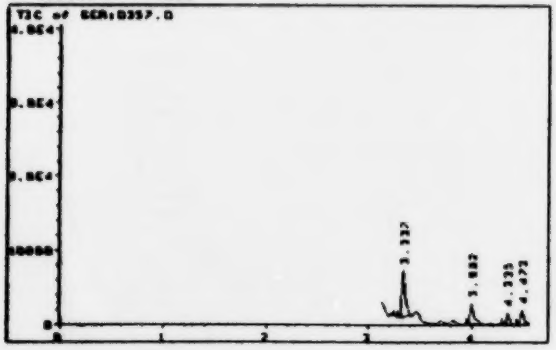


Figure 4:
Automatic Spectra Program: the 15 most prominent peaks;

```
Data file: SEA:D357.D
 File type: GC / MS DATA FILE

 Name Info: UN-DERIVATIZED STANDARD  X 2UL
 Misc Info: **MOEDS3.M**  NEW TEMPERATURE PROGRAM
 Operator : DS

 Date     :  5 Jul 85  12:49 pm
 Instrment: MS_5970
 Inlet    : GC

 Sequence index :    2
 Als bottle num :   99
 Replicate num  :    1
```



```
Scan 17 (3.342 min) of SEA:D357.D
SEA:D357.D
     m/z      abund.     m/z      abund.     m/z      abund.     m/z      abund.
    51.10        220    52.20         79    53.00        153    55.00        290
    56.10        171    57.00        313    61.00        129    62.00        189
    63.00        259    64.20         96    65.00        752    66.10       1258
    67.00         94    74.00         85    91.10         84    92.10         95
    93.10        366    94.00       2613    95.00        182
Scan 66 (3.988 min) of SEA:D357.D
SEA:D357.D
     m/z      abund.     m/z      abund.     m/z      abund.     m/z      abund.
    51.00        132    53.00        166    56.00        127    57.00        189
    71.10         79    77.00        293    79.00        298    80.10         95
    89.10         86    90.10        108    91.00        106   107.10        535
   108.00        602
Scan 92 (4.331 min) of SEA:D357.D
SEA:D357.D
     m/z      abund.     m/z      abund.     m/z      abund.     m/z      abund.
    55.10        150    56.10        126    57.00        668    58.10         94
    70.10         94    71.00        292    85.10         95    91.10         88
Scan 103 (4.476 min) of SEA:D357.D
SEA:D357.D
     m/z      abund.     m/z      abund.     m/z      abund.     m/z      abund.
    51.00        246    77.10        653   118.10        701   119.10         80
   133.00        251
```



```
Scan 157 (5.186 min) of SEA:D357.D
SEA:D357.D
     m/z      abund.     m/z      abund.     m/z      abund.     m/z      abund.
    51.10       1258    51.90        183    61.00        158    62.10        314
    63.00        777    64.10        679    72.90         78    74.10        636
    75.00        589    76.00        378    77.00        606    78.10        328
    86.00        147    87.00        156    98.00        177    99.00         82
   100.00         95   101.10        350   102.00       1154   103.00         96
   126.10        781   127.10       1488   128.10      10284   129.00       1179
Scan 556 (10.464 min) of SEA:D357.D
```

Figure 5:

MANN LINK

A SOFTWARE PROGRAM DEVELOPED FOR THE

MOE/HOC PROJECT

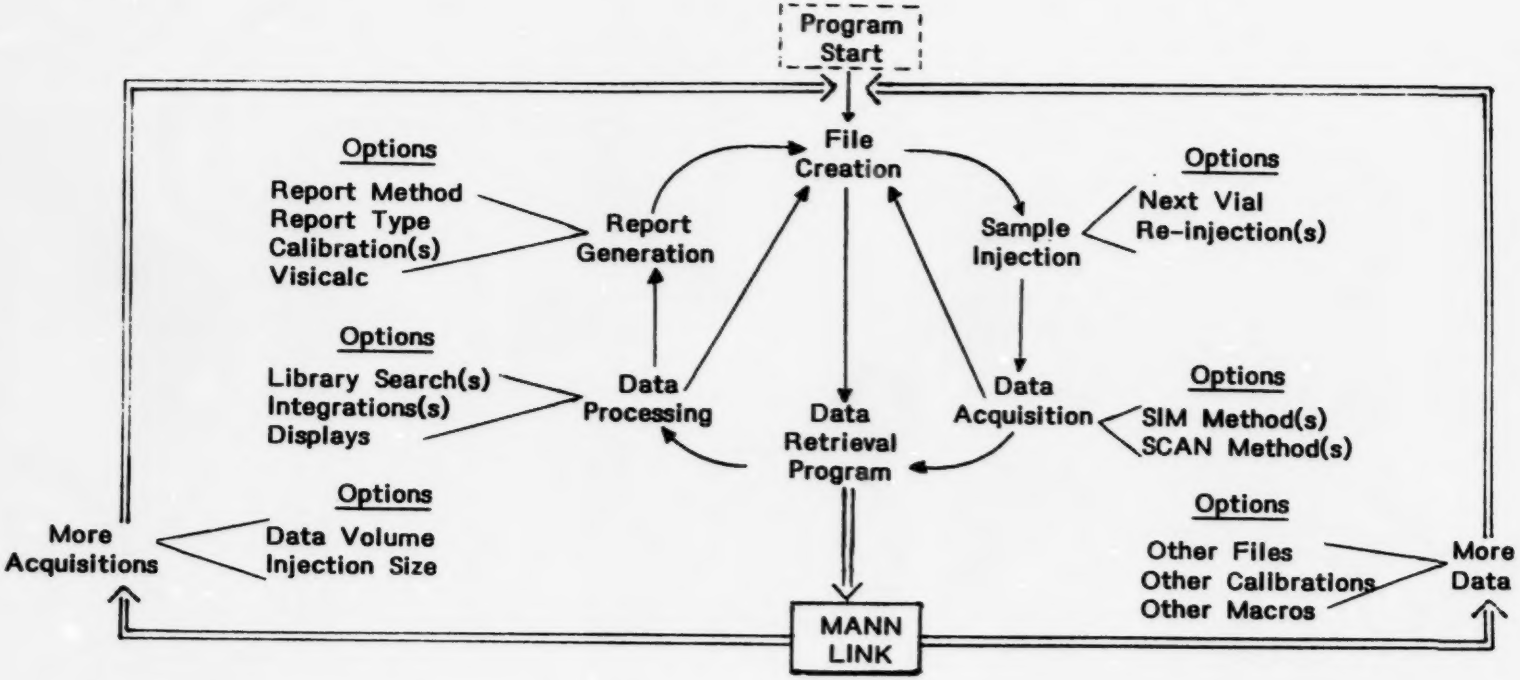
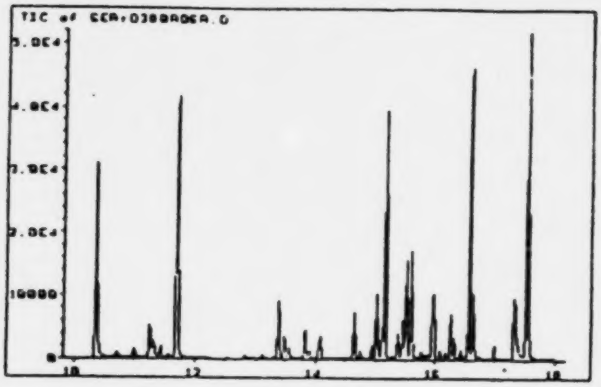

Program Start
File Creation
Options
Report Method
Report Type
Calibration(s)
Visicalc
Report Generation
Sample Injection
Options
Next Vial
Re-injection(s)
Options
Library Search(s)
Integrations(s)
Displays
Data Processing
Data Retrieval Program
Data Acquisition
Options
SIM Method(s)
SCAN Method(s)
Options
More Acquisitions
Data Volume
Injection Size
Options
Other Files
Other Calibrations
Other Macros
More Data
MANN LINK

Figure 6:

Arochlor 1254: visual pattern recognition;



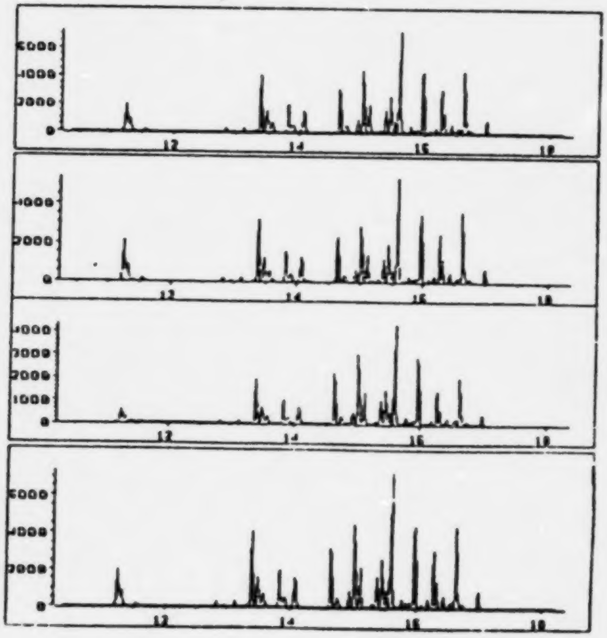
for the following four chromatograms

tic #1 = quantitation ions for pcb 1254

tic #2 = qualifier #1 ions for pcb 1254

tic #3 = qualifier #2 ions for pcb 1254

tic #4 = quantitation ions from pcb 1254 standard



following criteria:

i) the strict adherence to the correct relative retention time window with respect to the two time reference peaks

ii) the presence of the designated quantitation ion and two qualifying ions

iii) the correct ion ratios of the two qualifiers to the quantition ion

iv) the peak area of the internal standard must be within a specific tolerence

Following these acquisitions and reports, further data reduction macros were automatically envoked to display ions and qualifiers for Aroclor 1254. Special programming displayed Aroclor 1254 in such a way as to allow visual pattern recognition by the operator similar to that being done with the electron capture detector. Several options then followed: library search for a number of peaks or every peak in the chromatogram; display spectra of every peak; continue injection of the same batch of samples or process another batch using different macros; transfer the data to another media and delete the file on hard disk.

In every aspect these types of software development are to allow complete flexibility and to achieve maximum sample throughput .

CONCLUSIONS

Based on the results obtained from the two approaches, in-situ acetylation and extraction coupled with the purge and trap method , amd thermal stripping technique, it is clear that the former approach offers better reliability and accuracy and is a significant improvement over the existing protocol for analysis of these sample matricies.

It is a simple, less labour intensive and less time consuming extraction procedure. Sufficient sample throughput has also been achieved through automation via the Mass Selective Detector and it's highly flexible data system. Recoveries and their statistical reliability have been maintained or in most cases are better than the existing protocol.

The thermal stripping approach shows promise but needs more extensive development. For this project the In-Situ Acetylation/ Purge and Trap approach was judged as the method of choice. Further investigations will continue into the ruggedness of this method.

Efforts will also be continued to create more efficient data processing and reporting approaches, and Pascal programming will be used to develop a more user friendly interface.

ACKNOWLEDGEMENTS

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Valuable suggestions offered by Dr. Pierre Beaumier are gratefully acknowledged.

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ANALYSIS OF CHEMICALS USED AT WATER TREATMENT PLANTS

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Key words: Organic Analysis, Water Treatment Chemicals, GC-MS.

ABSTRACT

The objective of this study was to develop analytical methodology for the isolation and identification of trace organic contaminants present in inorganic water treatment chemicals. This work included the development of extraction techniques in which the organic compounds are separated from the largely inorganic sample matrix. Further separation and identification of the organic compounds in the final extracts was carried out using combined gas chromatographic/mass spectrometric techniques.

A wide variety of the chemicals most commonly used in the water treatment process were studied. These chemicals are used in processes such as coagulation, pH adjustment, corrosion control, water softening, and fluoridation. The chemicals studied were classified into two distinct groups, each of which required a different extraction procedure. Solid samples were extracted using Soxhlet extraction techniques, while sample preparation for the aqueous solutions involved liquid-liquid extraction with a suitable organic solvent.

Compound identifications were made using GC/MS techniques in which two ionization modes were employed. Electron impact ionization was used for obtaining structural information, while chemical ionization using methane as the reagent gas was used for molecular weight determination.

The organic contaminants which were identified consisted of compounds such as: straight-chain alcohols, carboxylic acids, and alkenes; aliphatic and phthalate esters; cyclic ketones, alcohols, and alkenes; phenolic compounds and other substituted aromatic compounds; and compounds containing nitrogen and/or sulphur. The majority of these contaminants are simple hydrocarbons, while chlorinated species are virtually absent with only three identified. The total organic content in the chemicals studied was found to range between 0.01 and 300 ppm, with the majority of these samples containing less than 10 ppm of organic contaminants.

ABSTRACT

Methodology is developed for the isolation and identification of organic constituents present in inorganic water treatment chemicals. Solid and liquid samples are analyzed by gas chromatography/mass spectrometry using two complementary ionization techniques, electron impact (EI) and positive ion chemical ionization (PICI). Actual samples representative of the most commonly employed water treatment chemicals were obtained from a variety of sources. The majority of the organic contaminants found to be present in these samples contain only carbon, hydrogen, oxygen, and in some cases nitrogen. In the twenty-four samples analyzed only a total of three chlorinated species were identified. The total organic content of the various chemicals studied was found to range from 0.01 to 300 parts-per-million (ppm), however, most samples contained less than 10 ppm.

INTRODUCTION

Testing of the quality of drinking water is performed on a routine basis in many North American cities. The majority of the research carried out is devoted to the development and improvement of methods for the determination of either organic or inorganic species in the final product of the water purification process (1-8). However, it is also important that the sources of any contaminants be recognized so that measures can be taken to reduce the presence of these materials. This study is concerned with the development of methodology for the isolation and identification of trace organic contaminants present in the inorganic chemicals typically employed in the water treatment process. This methodology is then used to analyze a series of chemicals actually utilized for water treatment.

The use of gas chromatographic/mass spectrometric (GC/MS) techniques have proven to be very useful in the analysis of complex organic mixtures. The mass spectrometer is an ideal detector for the gas chromatograph because of its sensitivity and specificity. Unlike detectors more commonly used, such as flame ionization and electron capture detectors (FID and ECD respectively), the mass spectrometer can supply a tremendous amount of information regarding the structure of each individual analyte. Thus in a single GC/MS run it is possible to obtain information about the structure and retention time behaviour of a particular component.

Compound identifications in this study are based mainly on the comparison of the EI mass spectrum of the unknown component with the spectra of a large number of reference compounds. This process is carried out by the computer data system using the Probability Based Matching (PBM) algorithm (9). However, because there are many cases where compounds give very nearly identical EI mass spectra, identifications based on this information were supplemented with data from a second ionization technique, positive ion chemical ionization (PICI), a so-called "soft" ionization technique in which relatively little fragmentation is observed using methane as the reagent gas (10). Therefore it is often possible to obtain molecular weight information which may have been lacking or inconclusive based on the corresponding EI mass spectrum. By combining the complementary information obtained from the EI and PICI techniques with retention time data for any available standards (which can often be used to differentiate between isomers), positive compound identifications can be made.

The analytical methodology developed and used in this study for the analysis of trace organic contaminants in water treatment chemicals is outlined in the flow diagram shown in figure 1.

EXPERIMENTAL

Chemicals

The solvents used in this study were dichloromethane and methanol (distilled-in-glass; Caledon Laboratories Ltd., Ontario, Canada). Anhydrous sodium sulphate (reagent grade; J.T. Baker Chemical Co., Phillipsburg, New Jersey) was purified by means of sequential Soxhlet extraction with methanol followed by dichloromethane. The purified sodium sulphate was then stored in a stoppered glass flask and kept in an oven heated to 200 °C.

The methane used as the reagent gas in the chemical ionization studies was ultrahigh purity grade (Union Carbide Canada Ltd., Ontario, Canada).

Standard solutions used for obtaining retention time data as well as mass spectra for the user-created data base were made up using standards available from the PolyScience Corporation (Chemical Division, Niles, Illinois) and from a variety of other commercial sources.

Glassware Cleaning

In the analysis of trace organic compounds, special precautions must be taken to ensure that contamination of the sample does not occur during the sample preparation procedure. It is therefore necessary to clean any glassware which comes in contact with the sample to be analyzed. The glassware used in this study was washed in an ultrasonic bath with a mild detergent for approximately thirty minutes. Individual pieces are then rinsed with copious quantities of deionized water and dried overnight in an oven at 275 °C. All glassware is rinsed three times with dichloromethane immediately before use. Soxhlet extraction apparatus is rinsed by setting the equipment up in the normal fashion and extracting the empty apparatus with 300 mL of dichloromethane for two hours.

Sample Preparation

All solid samples were extracted for 30 hours with 300 mL of dichloromethane using Soxhlet extraction apparatus. Each sample was extracted in duplicate and a blank was also run using a complete but empty extraction apparatus. The amount of solid extracted was set by the volume limitations of the extraction thimbles used and was found to be approximately 100 cm^3 for efficient extraction. After the extraction period had elapsed, the resulting organic mixture was then concentrated down to approximately 1 mL using rotary evaporation. The extract was then transferred, rinsing the collection flask with dichloromethane, to a small glass vial such that the total volume of the extract and rinsings was about 5 mL.

A 500 mL volume of liquid sample is extracted with three 100 mL aliquots of dichloromethane using a 1-litre separatory funnel. The combined extract is then passed through a sintered glass crucible containing approximately 20 grams of purified sodium sulphate in order to remove any traces of water which may be present. The sodium sulphate is then rinsed with 50 mL of fresh dichloromethane once the entire sample extract has been passed through it. The resulting organic mixture is then concentrated and transferred to a small glass vial giving a final volume of approximately 5 mL.

Unlike the other liquid samples which were analyzed, hydrofluorosilicic acid can be particularly hazardous to work with because it shows many of the same chemical properties as hydrofluoric acid. Its corrosiveness towards glassware requires that polypropylene separatory funnels be used in place of the conventional glass appparatus. The hydrofluorosilicic acid samples are otherwise extracted using the same procedure employed for the other liquid samples.

Some of the inorganic salts found in the water treatment chemicals show a limited solubility in dichloromethane. This can cause considerable problems in the chromatographic analyses as these salts are retained on the column due to their high boiling points and here they act as active sites. These active sites result in the broadening of peak shapes for compounds which are even slightly polar in nature. As a result of this, a cleanup procedure is necessary prior to analysis by GC/MS.

Each concentrated extract is passed through a Sep-Pak silica cartridge (Millipore Waters Associates, Milford, Massachusetts) which has been pre-wet with 10 mL of dichloromethane. This is accomplished using a 50 mL gas-tight syringe with a Luer end fitting. The inorganic salts are irreversibly adsorbed on the polar stationary phase while the organics are eluted by passing 50 mL of dichloromethane through the cartridge. The eluate is collected and concentrated down to about 1 mL using rotary evaporation. The extract is then transferred to a precalibrated vial and concentrated down to a final volume of 100 microliters using a gentle stream of high purity nitrogen gas (Union Carbide Canada Ltd., Ontario, Canada).

Instrumentation

All analyses were carried out using a Hewlett-Packard HP5987A gas chromatograph/mass spectrometer equipped with an HP1000 data system and an HP7914 Winchester disk drive. An HP5880A gas chromatograph is linked to the quadrupole mass spectrometer by a direct capillary inlet interface such that all of the column effluent enters the ion source. Chromatographic separations were obtained using a 30 meter fused silica Supelcowax 10 capillary column (Supelco Canada Ltd., Oakville, Ontario, Canada) which had a film thickness of 0.25 um and a 0.25 mm I.D. Helium was used as the carrier gas with a flow rate of 1.1 mL/min. A cool on-column injector was employed in all chromatographic analyses in order to minimize discrimination against both low and high boiling point compounds. The GC oven temperature program used was as follows: initial temperature 45 ^{o}C ramped at 3 ^{o}C/min to a final temperature of 270 ^{o}C which was then held for 15 minutes.

The HP5987A GC/MS system has capabilities for several different ionization modes including electron impact (EI), positive ion chemical ionization (PICI), and negative ion chemical ionization (NICI). In EI operation the mass spectrometer is tuned using an automatic tuning program known as AUTOTUNE which is provided by Hewlett-Packard. This program adjusts the mass spectrometric parameters to meet the predetermined performance criteria using the reference compound perfluorotributylamine (PFTBA). In PICI, however, the mass spectrometer must be manually tuned using the reference compounds benzophenone and PFTBA. The various mass spectrometric parameters are optimized while monitoring the $[M+H]^+$ ion (m/z 183) of benzophenone. The mass axis is then calibrated using m/z 183 from benzophenone and two ions from methane PICI mass spectrum of PFTBA, m/z 414 and 652.

The mass spectrometric parameters for both ionization techniques are summarized in table I.

The GC/MS data system employed in this study utilizes two different mass spectral data bases in its computerized search program. The data base available from the instrument supplier is made up from the NIH/EPA/MSDC Mass Spectral Data Base (NBS Library) and the Registry of Mass Spectral Data (Wiley Library). This data base contains 76,862 mass spectra, some of which are the same compound run on a different spectrometer. In addition to the NBS/Wiley data base, a user-created data base consisting of mass spectra acquired on our instrument was also established. Using the search algorithm supplied with the data system it is possible to search these data bases consecutively in a single search.

RESULTS AND DISCUSSION

The analytical methodology developed in this work has been shown to be applicable to the analysis of trace organic contaminants in inorganic chemicals such as those used by water treatment plants. A sample total-ion-current (TIC) chromatogram for one of the water treatment chemicals analyzed in this study is given in figure 2. As can be seen by the chromatogram, a fairly complex mixture of organic compounds can be extracted from the inorganic matrix. The methods developed for the analysis of water treatment chemicals should be applicable to most other inorganic compounds.

The total organic content of the samples analyzed was found to range from 0.01 to 300 ppm. For a given type of chemical there was little difference in the level of the contaminants present even for samples which were obtained from different manufacturers. It was also apparent that aqueous solutions of a given chemical had lower organic contents (in terms of ppm) than their corresponding solid samples. This is not too surprising in that there is a large difference in the weights of the solutions and solids which would be required to give the same dosage of the desired inorganic compound. However, because the concentrations of these solutions were not supplied, it is impossible to determine if the total organic content relative to the actual amount of the inorganic compound is approximately equal for the solid and liquid alums, for example. Some water treatment plants are equipped to utilize solutions of these chemicals while other plants may find it more convenient to work with the solid materials.

The organic contaminants which were identified consisted of compounds such as: straight-chain alkenes, alcohols, and carboxylic acids; aliphatic and phthalate esters; cyclic ketones, alcohols, and alkenes; phenolic compounds and other substituted aromatic compounds; and compounds containing nitrogen and/or sulphur. Almost all of these constituents are simple compounds (containing only carbon, hydrogen, and oxygen atoms) while chlorinated compounds are virtually absent with only three being identified. This is a significant fact because many chlorinated species have a high toxicity and therefore their presence is very undesirable. Although there were a wide variety of water treatment chemicals studied, there were many organic compounds or compound classes which appeared in several different chemicals. It is possible that these compounds may be introduced into the water treatment chemicals during their manufacturing, packaging, or transportation. One of the most commonly occurring compound classes are the phthalate esters which are found in many environmental samples (15). Because of their ubiquitousness in the environment, special care must be taken to ensure that they are not introduced into the sample during the preparation procedure.

It is also interesting to note that when two samples were obtained from the same supplier, there are many organic contaminants which could be identified in both samples. However, when samples of the same chemical were obtained from different suppliers there are differences in the types of contaminants present. This tends to support the previously suggested explanation for the occurrence of the organic contaminants in the water treatment chemicals.

Two of the hydrofluorosilicic acid samples which were analyzed consisted of samples which were taken from one batch with one being subjected to the manufacturer's cleanup procedure and the other remaining untreated. This cleanup reduced the total organic content by 50 percent, although it is interesting to note that some of the compounds appeared to be very effectively removed while others were only slightly reduced in quantity. Therefore the cleanup procedure shows some selectivity towards certain compounds in terms of the amount of contaminant which is removed.

TABLE I

EI and PICI Mass Spectrometric Conditions

Parameter	Ionization Mode	
	EI	PICI
source pressure (torr)	3×10^{-6}	1.6
source temperature (°C)	200	200
interface oven temperature (°C)	270	270
scan range (amu)	50 to 500	60 to 500
scan cycle time (msec)	0.92	0.78
scan increment size (amu)	0.125	0.125
scan start time (min)	2.80	2.80
A/D samples	4	4
emission current (uamps)	300	300
electron multiplier voltage (V)	2200	2200

TABLE II

Water Treatment Chemicals

CHEMICAL	ROLE IN TREATMENT PROCESS*	TYPICAL DOSAGE (ppm)**
alum (aluminum sulphate)	coagulant coagulant aid	15 - 150
ferric chloride	coagulant coagulant aid	5 - 120
hydrofluorosilicic acid	fluoridation	~ 1
lime (calcium oxide)	pH adjustment corrosion control water softening	5 - 15
polyelectrolytes	coagulant coagulant aid	0.05 - 150
soda ash (sodium carbonate)	pH adjustment corrosion control water softening	10 - 25
sodium hydroxide	pH adjustment corrosion control water softening	5 - 20
sodium silicates	coagulant coagulant aid corrosion control	~ 10
sodium silicofluoride	fluoridation	~ 1

* from references 11 and 12

** from references 11 to 14

TABLE III

Comparison of Compounds Identified in Solid Alum Samples

		SAMPLE #				
COMPOUND	MW	1	2	3	4	5
methylcyclopentane	84			X		
cyclohexanone	98		X		X	X
formic acid, cyclohexyl ester	128			X		
nonanal	142			X		
cyclohexanol	100		X		X	
2-hexen-1-ol	100					X
dihydro-5-methylfuranone	100			X		
2-chlorocyclohexanone	132			X		
dihydro-5-ethylfuranone	114			X		
8-chloro-1,4-dioxaspiro-[4,5]decane	176			X		
dihydro-5-propylfuranone	128			X		
cyclododecane	168		X			
dihydro-5-butylfuranone	142			X		
dodecanol	186	X	X			
dihydro-5-amylfuranone	156			X		

(cont'd)

TABLE III (cont'd)

		SAMPLE #				
COMPOUND	MW	1	2	3	4	5
isopropyl myristate	270	X				
hexanoic acid	116					X
butanoic acid, hexyl ester	172					X
heptanoic acid	130					X
octanoic acid	144				X	X
nonanoic acid	156				X	X
1,2-benzenedicarboxylic acid, diethyl ester	222	X				X
1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6-trione	249	X	X			
decanoic acid	172				X	X
1,3-di-t-butyl-2-hydroxy-5-methylbenzene	234		X			
octadecanol	270	X				
nonanedioic acid, dibutyl ester	300			X		
dodecanoic acid	200				X	X
1,2-benzenedicarboxylic acid, dibutyl ester	278	X	X			
undecanedioic acid, dibutyl ester	328			X		

(cont'd)

TABLE III (cont'd)

COMPOUND	MW	SAMPLE # 1	2	3	4	5
tetradecanoic acid	228				X	X
pentadecanoic acid	242					X
hexanedioic acid, dioctyl ester	370					X
hexadecanoic acid	256				X	X
heptadecanoic acid	270				X	X
octadecanoic acid	284				X	X
1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester	390	X	X	X		X
1,2-benzenedicarboxylic acid, diisooctyl ester	390					X
1,2-benzenedicarboxylic acid, dioctyl ester	390					X
1,2-benzenedicarboxylic acid, butyl phenylmethyl ester	312	X	X			X

alum #1: Alcan (Victoria Harbor)

alum #2: Allied Chemicals (Smith Falls)

alum #3: C.I.L. (Ear Falls)

alum #4: Allied Chemicals (Valleyfield)

alum #5: Allied Chemicals (Valleyfield)

TABLE IV

Comparison of Compounds Identified in Liquid Alum Samples

		SAMPLE #			
COMPOUND	MW	1	2	3	4
cyclohexanone	98			X	
cyclohexanol	100		X	X	
3-methyl-2-furanone	98		X	X	
3-methyl-2-norcaranone	124		X		
ethylcyclohexane	112		X	X	
undecanol	172	X			
2-methyl-1-penten-3-one	98		X	X	
sulfonylbismethane	94		X	X	
phenol	94				X
branched alcohol ($C_{14}H_{30}O$)	214	X			
tetrahydropyran-2-ol	102				X
branched alcohol ($C_{16}H_{34}O$)	242	X			
1-isobenzofuranone	134		X	X	
1,2-benzenedicarboxylic acid, diethyl ester	222		X	X	X
heptanedioic acid, dibutyl ester	272	X			
1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6-trione	249	X	X	X	X
branched alcohol ($C_{18}H_{38}O$)	270	X			

cont'd

TABLE IV (cont'd)

		SAMPLE #			
COMPOUND	MW	1	2	3	4
3,3'-oxybispropanenitrile	124			X	
nonanedioic acid, dibutyl ester	300	X			
octadecanol	270			X	
branched alcohol ($C_{20}H_{42}O$)	298	X			
1,2-benzenedicarboxylic acid, dibutyl ester	278	X	X	X	X
4-hydroxybenzaldehyde	122				X
undecanedioic acid, dibutyl ester	328	X			
branched alcohol ($C_{22}H_{46}O$)	326	X			
tridecanedioic acid, dibutyl ester	356	X			
1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester	390	X	X	X	X
1,2-benzenedicarboxylic acid, diheptyl ester	362				X
1,2-benzenedicarboxylic acid, butyl phenylmethyl ester	312		X	X	X
1,2-benzenedicarboxylic acid, dioctyl ester	390				X
1,2-benzenedicarboxylic acid, dinonyl ester	418				X
1,2-benzenedicarboxylic acid, didecyl ester	446				X

alum #1: Alcan (Huntsville)

alum #2: Allied Chemicals (Deseronto)

alum #3: Allied Chemicals (Deep River)

alum #4: Allied Chemicals (Thorold)

TABLE V

Comparison of Compounds Identified in Polyelectrolytes

COMPOUND	MW	SAMPLE # 1	2	3
chloroform*	118	X	X	
octanol	130			X
decanoic acid, methyl ester	186			X
hexadecene	224			X
decanol	158			X
dodecanoic acid, methyl ester	214			X
octadecene	252			X
tetradecanoic acid, methyl ester	242			X
2-propenamide	71	X		
hexadecanoic acid, methyl ester	270			X
tetradecyne	194		X	
1,1'-[oxybis(methylene)]bisbenzene	198			X
5-ethyl-2-methyl-5-hepten-3-one	154	X		
octadecenoic acid, methyl ester	296			X
benzoic acid, phenylmethyl ester	212			X
3,3'-oxybispropanenitrile	124	X		
3,3'-iminobispropanenitrile	123	X		
1,2-benzenedicarboxylic acid, dibutyl ester	278	X		X

cont'd

TABLE V (cont'd)

COMPOUND	MW	SAMPLE # 1	2	3
hexadecanoic acid	256	X		
hexanedioic acid, dioctyl ester	370		X	
octadecanoic acid	284	X		
1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester	390	X		X
1,2-benzenedicarboxylic acid, butyl phenylmethyl ester	312	X		
spectra-sorb UV 531 ($C_{21}H_{26}O_3$)	326			X

* impurity in dichloromethane

polyelectrolytes #1: unknown

polyelectrolytes #2: Calgon (Toronto)

polyelectrolytes #3: Allied Colloids (USA)

TABLE VI

Comparison of Compounds Identified in Hydrofluorosilicic Acid

COMPOUND	MW	SAMPLE # 1	2	3
2,4,6-trimethyloctane	156	X	X	X
chloroform*	118		X	X
branched alkane ($C_{11}H_{24}$)	156	X		
acetic acid	60	X	X	X
propanoic acid	74	X	X	X
2,2-dimethylpropanoic acid	102		X	X
butanoic acid	88			X
3,4-dimethyl-2,5-furandione	126	X		
pentanoic acid	102			X
4,5,5-trimethyl-2-furanone	126	X	X	X
3-ethyl-4-methyl-3-penten-2-one	126		X	
1-cyclohexylethanone	126	X		
hexanoic acid	116			X
2,3-dimethyl-2-butenoic lactone	112	X	X	
2,6-bis(1,1-dimethylethyl)-4-methylphenol	220	X		X
cyclododecane	168	X		X
di-t-butylhydroxyanisole	236	X	X	X
2-hydroxy-3,5,5-trimethyl-2-cyclohexenone	154	X		

cont'd

TABLE VI (cont'd)

COMPOUND	MW	SAMPLE # 1	2	3
hexadecyloxyethanol	286		X	
benzoic acid	122	X		X
1-methyl-2,4-dinitrobenzene	182	X		
3-methylbenzoic acid	136			X
benzeneacetic acid	136			X
octadecanol	270	X	X	X
eicosatriene	276		X	X
tetradecanoic acid	228		X	
hexadecanoic acid	256	X	X	X
octadecanoic acid	284	X	X	X

* impurity in dichloromethane

hydrofluorosilicic acid #1: C.I.L. (Lampton Works)

hydrofluorosilicic acid #2: C.I.L. (Lampton Works)**

hydrofluorosilicic acid #3: C.I.L. (Lampton Works)

** same batch as the first sample but passed through a cleanup procedure by the manufacturer

TABLE VII

Total Content of Trace Organic Contaminants

CHEMICAL	SOURCE	TOC* (ppm)
alum**	Alcan (Victoria Harbor)	1
alum**	Allied Chemicals (Smith Falls)	0.9
alum**	C.I.L. (Ear Falls)	0.9
alum**	Allied Chemicals (Valleyfield)	1
alum**	Allied Chemicals (Valleyfield)	6
sodium silicates	National Silicates (Toronto)	0.02
sodium silicates	National Silicates (Toronto)	0.03
soda ash**	Allied Chemicals (Deep River)	2
soda ash**	Allied Chemicals (Amherstburg)	0.8
sodium bicarbonate**	Allied Chemicals (Alexandria)	0.04
sodium silicofluoride**	Supertos (Owen Sound)	1
sodium hydroxide	C.I.L. (Lindsay)	0.09
lime**	Domtar (Beachville)	300
alum	Alcan (Huntsville)	0.2
alum	Allied Chemicals (Deseronto)	0.01

cont'd

TABLE VII (cont'd)

CHEMICAL	SOURCE	TOC* (ppm)
alum	Allied Chemicals (Deep River)	0.01
alum	Allied Chemicals (Thorold)	0.01
polyelectrolytes	unknown	0.01
polyelectrolytes	Calgon (Toronto)	0.02
polyelectrolytes**	Allied Colloids (USA)	8
ferric chloride	Diversey	0.03
hydrofluorosilicic acid	C.I.L. (Lampton Works)	40
hydrofluorosilicic acid	C.I.L. (Lampton Works)***	20
hydrofluorosilicic acid	C.I.L. (Lampton Works)	9

* approximate total organic content

** solid samples

*** same batch as the first hydrofluorosilic acid sample but passed through a carbon adsorber (manufacturer's cleanup procedure)

FIGURE 1: Analytical scheme for the isolation and identification of trace organic contaminants in water treatment chemicals.

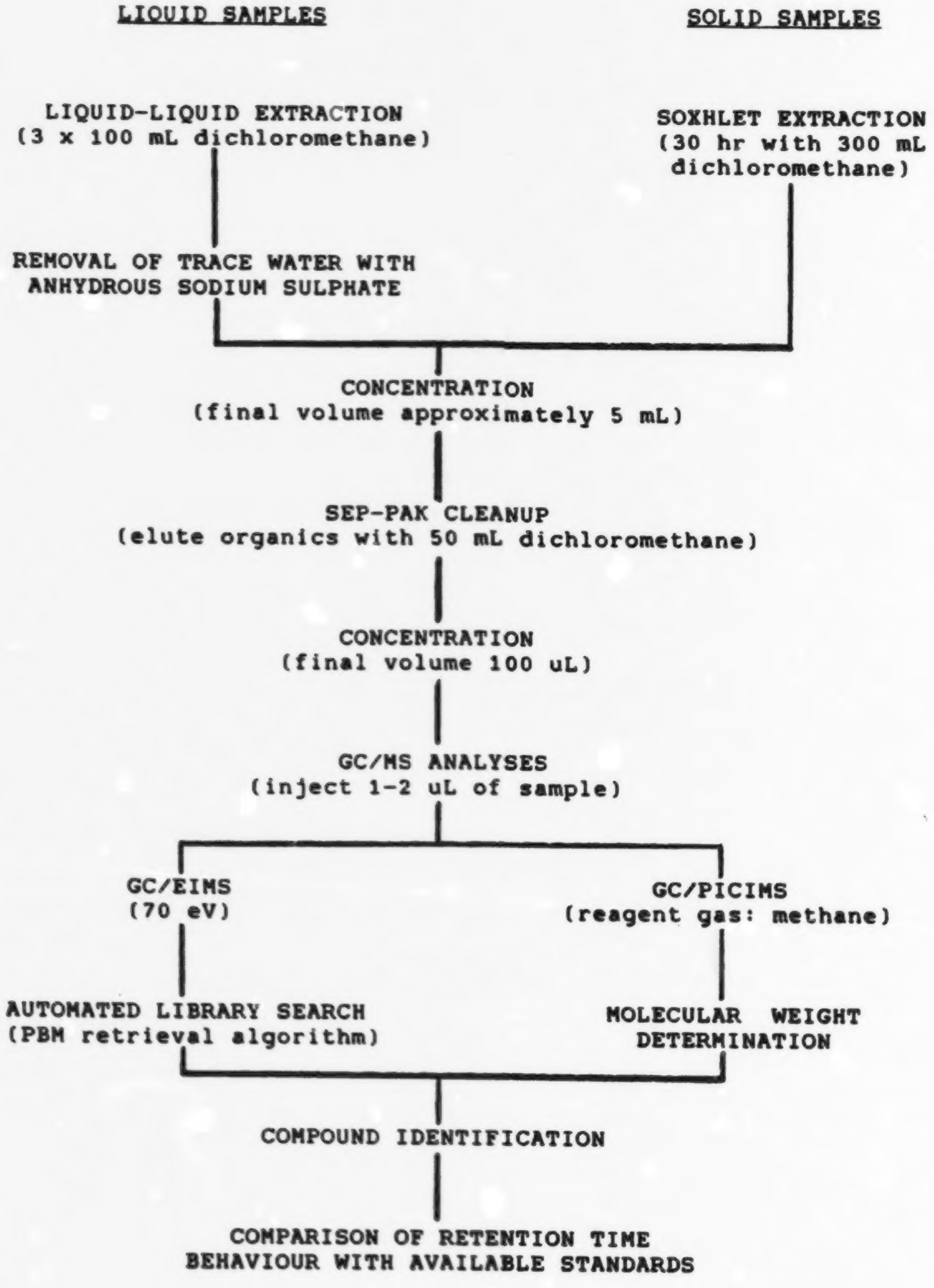
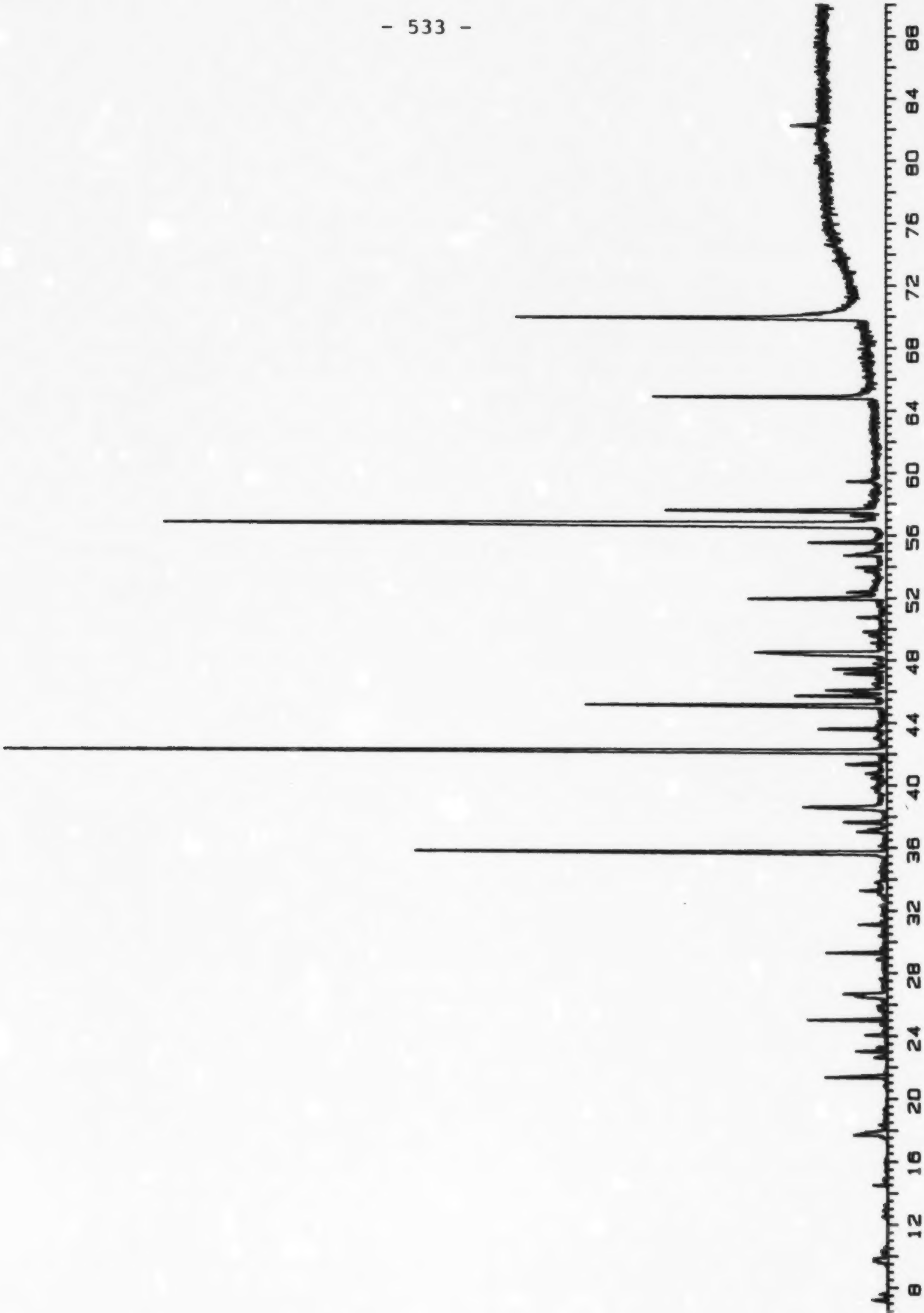

LIQUID SAMPLES
SOLID SAMPLES
LIQUID-LIQUID EXTRACTION (3 x 100 mL dichloromethane)
SOXHLET EXTRACTION (30 hr with 300 mL dichloromethane)
REMOVAL OF TRACE WATER WITH ANHYDROUS SODIUM SULPHATE
CONCENTRATION (final volume approximately 5 mL)
SEP-PAK CLEANUP (elute organics with 50 mL dichloromethane)
CONCENTRATION (final volume 100 uL)
GC/MS ANALYSES (inject 1-2 uL of sample)
GC/EIMS (70 eV)
GC/PICIMS (reagent gas: methane)
AUTOMATED LIBRARY SEARCH (PBM retrieval algorithm)
MOLECULAR WEIGHT DETERMINATION
COMPOUND IDENTIFICATION
COMPARISON OF RETENTION TIME BEHAVIOUR WITH AVAILABLE STANDARDS

FIGURE 2: TIC trace of hydrofluorosilicic acid extract (for GC/MS operating conditions see text).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